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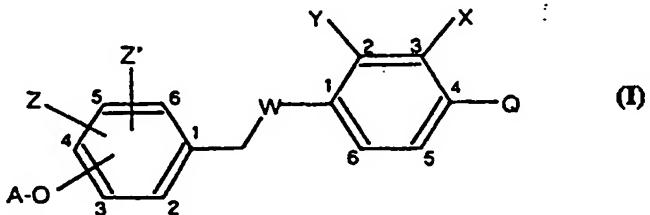
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : A01N 43/54, C07D 239/54	A1	(11) International Publication Number: WO 97/08953 (43) International Publication Date: 13 March 1997 (13.03.97)
(21) International Application Number: PCT/US96/14193		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 5 September 1996 (05.09.96)		
(30) Priority Data: 08/523,991 5 September 1995 (05.09.95) US		
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(54) Title: HERBICIDAL 2-[(4-HETEROCYCLIC-PHOXYMETHYL)PHENOXY]-ALKANOATES

(57) Abstract

Herbicidal compounds, compositions containing them, and a method for controlling weeds by application of the compositions are disclosed. The herbicidal compounds are 2-[(4-heterocyclic-phenoxymethyl)phenoxy]-alkanoates of formula (I), in which A is a derivative of an alcanoate bonded to the phenoxy oxygen at the alpha carbon, and Q is 4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl, 3,4,5,6-tetrahydronaphthalimid-1-yl, 1-(1-methylethyl)imidazolidin-2,4-dion-3-yl, 1,4-dihydro-4-(3-fluoropropyl)-5H-tetrazol-5-on-1-yl, 3-chloro-4,5,6,7-tetrahydroindazol-2-yl, 4-methyl-1,2,4-triazine-3,5-dion-2-yl, 8-thia-1,6-diazabicyclo[4.3.0]nonane-7-on-9-ylimino, or 1-methyl-6-trifluoromethyl-2,4-pyrimidinedione-3-yl; X is hydrogen, methyl, fluorine, or chlorine; Y is hydrogen; W is oxygen or sulfur; Z is hydrogen, fluorine, chlorine, bromine, lower alkyl, or methoxy; Z' is hydrogen, fluorine, or chlorine; and the group AO- may be in the 2, 3, or 4-position of the phenyl ring.



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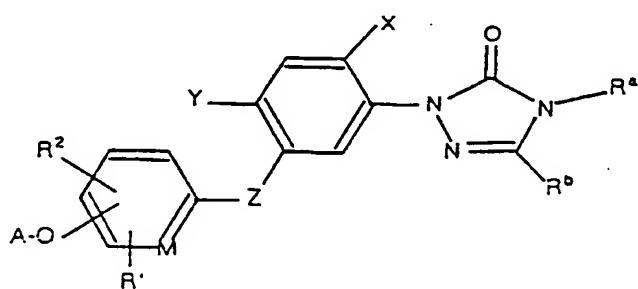
HERBICIDAL 2-[(4-HETERO CYCLIC-PHENOXYMETHYL) PHENOXY]-ALKANOATES

This invention pertains to novel herbicidal 2-[(4-heterocyclic-substituted-3-halophenoxy)methyl]phenoxy-alkanoates, especially propionates and acetates, and their use for weed control in agriculture, horticulture, and other fields in which it is desired to control unwanted plant growth, such as grassy or broadleaf plant species. In particular, it pertains to those compounds in which the heterocyclic moiety is selected from among 4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl; 3,4,5,6-tetrahydro-phthalimid-1-yl, 1-(1-methylethyl)imidazolidin-2,4-dion-3-yl; 1,4-dihydro-4-(3-fluoropropyl)-5H-tetrazol-5-on-1-yl; 3-chloro-4,5,6,7-tetrahydroindazol-2-yl; 4-methyl-1,2,4-triazine-3,5-dion-2-yl; 8-thia-1,6-diazabicyclo[4.3.0]nonane-7-on-9-ylimino; and 1-methyl-6-trifluoromethyl-2,4-pyrimidinedione-3-yl groups.

These compounds are both pre- and postemergence herbicides. The use of this class of compounds as herbicides has not previously been described.

U.S. 5,084,085 discloses compounds of the formula:

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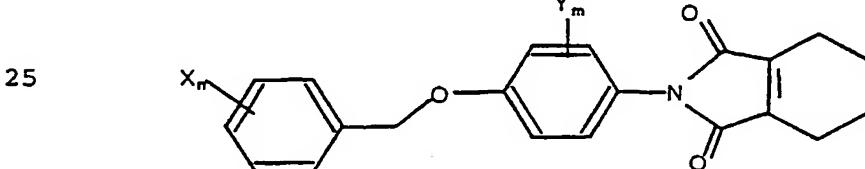
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- 2 -

wherein
R^a is preferably lower haloalkyl, and R^b is
preferably lower alkyl;
R' and R² are broadly defined;
5 X and Y are independently halogen, alkyl, alkoxy,
alkylthio, haloalkyl, nitro, cyano, sulfonylalkyl,
or -SOCF₃;
M is CH or N; and
A is a derivative of an alkanoate bonded to the
10 phenoxy oxygen at the alpha carbon.

U.S. 4,816,065 discloses compounds like those of
U.S. 5,084,085, except that the triazolinone ring has
been replaced by a 3,4,5,6-tetrahydropthalimido
moiety. Similarly, U.S. 4,885,025 discloses compounds
15 in which the triazolinone ring of U.S. 5,084,085 has
been replaced with a tetrazolinone moiety.

U.S. 3,984,434, Japanese patents 54-25018, 54-
26534, and 60-39668, and Japanese patent applications
49-000432 and 54-19965, all assigned to Mitsubishi
20 Chemical Industries, Ltd., disclose compounds of the
general formula:



wherein
X is hydrogen, halogen, nitro, alkyl, or alkoxy,
30 Y is hydrogen, halogen, alkyl, and n and m are each
1 to 4.

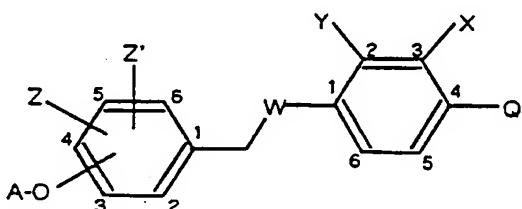
It has now been found that 2-[(4-heterocyclic-
substituted-3-halophenoxy)methyl]phenoxyalkanoates are
unexpectedly active as both pre- and postemergence
35 herbicides. In particular, as preemergence herbicides
many of these compounds exhibit tolerance of soybeans

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and, to a certain extent, of corn. Perhaps of greater interest is the postemergence activity, where no crop tolerance is exhibited, making them excellent candidates as total vegetation control agents.

5 The novel 2-[(4-heterocyclic-substituted-3-halo-phenoxy)methyl]phenoxyalkanoates of the present invention are described by the following generic structure:

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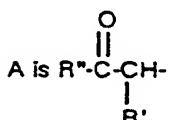


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Chemical Structure I

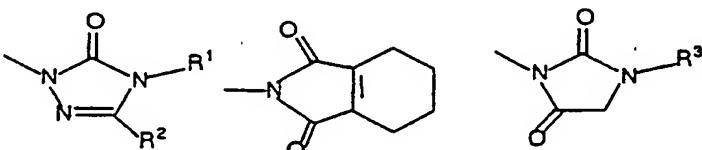
wherein

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Q is selected from the following heterocycles:

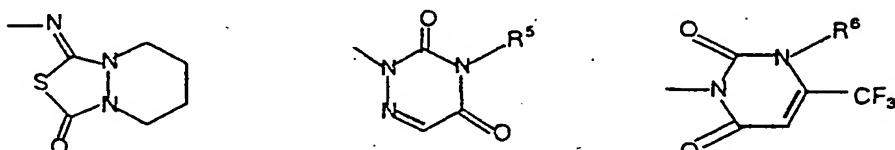
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W is oxygen or sulfur;
X is selected from hydrogen, methyl, fluorine, or chlorine;
Y is hydrogen, or
5 X and Y taken together may be $-O-C(CH_3)_2CH_2-$ to form a 7-substituted-4-benzofuranyl moiety;
R' is hydrogen or methyl;
R'' is -OR or amino, arylamino (e.g. phenylamino),
10 alkylamino (e.g. lower alkylamino such as methylamino or dimethylamino), alkenylamino (e.g. lower alkenylamino such as diallylamino), alkoxyamino (e.g. lower alkoxyamino such as methoxyamino); cyano, or alkyl-, haloalkyl-, or arylsulfonylamino of the formula $-N(lower alkyl)SO_2R^9$, or $-NHSO_2R^9$;
15 R is hydrogen, M, alkyl (e.g., lower alkyl such as methyl or ethyl), cycloalkyl, lower alkenyl or lower alkynyl, each optionally substituted with one or more chlorine or fluorine, or
20 $-[CHR^7(CH_2)_mO]_nR^8$,
each of R¹ through R⁶ is lower alkyl or lower haloalkyl;
R⁷ is hydrogen or lower alkyl;
R⁸ is alkyl, preferably lower alkyl;
25 R⁹ is alkyl (e.g. lower alkyl such as methyl, ethyl or propyl), haloalkyl (e.g. halo lower alkyl such as trifluoromethyl), or aryl such as phenyl or substituted phenyl, (e.g. lower alkoxy-substituted and/or halo-substituted phenyl);
30 m is 0 to 2, preferably 0 to 1, and n is 1 to 6, preferably 1 to 3; and
M is a monovalent, salt-forming group such as sodium, potassium, or ammonium;
Z is hydrogen, fluorine, chlorine, bromine, lower alkyl, phenyl, or methoxy;
35 Z' is hydrogen, fluorine, or chlorine; or

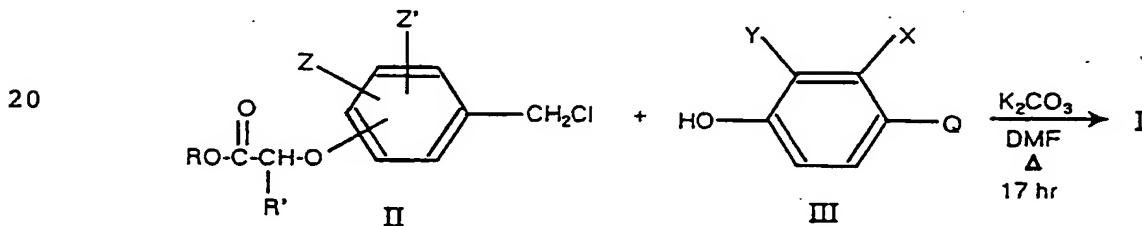
- 5 -

Z and Z' taken together may be $-(CH_2)_4-$ to form a tetrahydronaphthyl moiety; and the group A-O- may be in the 2, 3, or 4-position of the phenyl ring.

5 Preferred compounds are those in which R" is -OR and Z is chlorine or lower alkyl.

Particularly preferred are those compounds in which R is lower alkyl, lower chloroalkyl, or $-[CHR^7-$ $(CH_2)_mO]nR^8$; R¹ is difluoromethyl; R² is methyl; R³ is 10 1-methylethyl; R⁴ is 3-fluoropropyl; R⁵ is methyl; R⁶ is methyl; R⁷ is H or CH₃; R' is methyl; Z is in the 4-position; Z' is hydrogen or chlorine in the 3-position; m is 0 or 1, and n is 1 to 3; and the group AO- is in the 2-position 15 of the phenyl ring.

Many of the compounds of the invention were prepared by the following reaction:

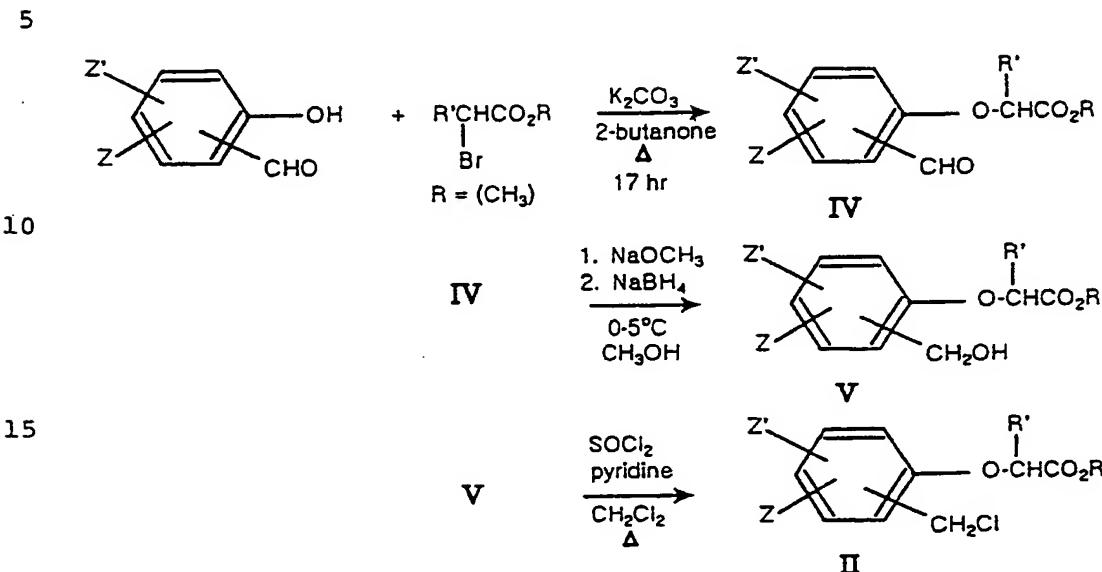


An appropriately substituted methyl 2-(chloromethylphenoxy)alkanoate and an appropriately substituted 4-heterocyclic-substituted phenol were heated in N,N-dimethylformamide at 80°C in the presence of at least a molar equivalent of potassium carbonate. Usually the reaction was run overnight. Preparation of 30 the corresponding acid (R=H) was accomplished by hydrolyzing the ester with aqueous sodium hydroxide and then acidifying the product with hydrochloric acid. For those compounds in which R is 2-(2-methoxyethoxy)-ethyl, transesterification of the methyl ester with 2- 35 (2-methoxyethoxy)ethanol in the presence of titanium (IV) isopropoxide was utilized.

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Intermediates were prepared according to the following schemata:

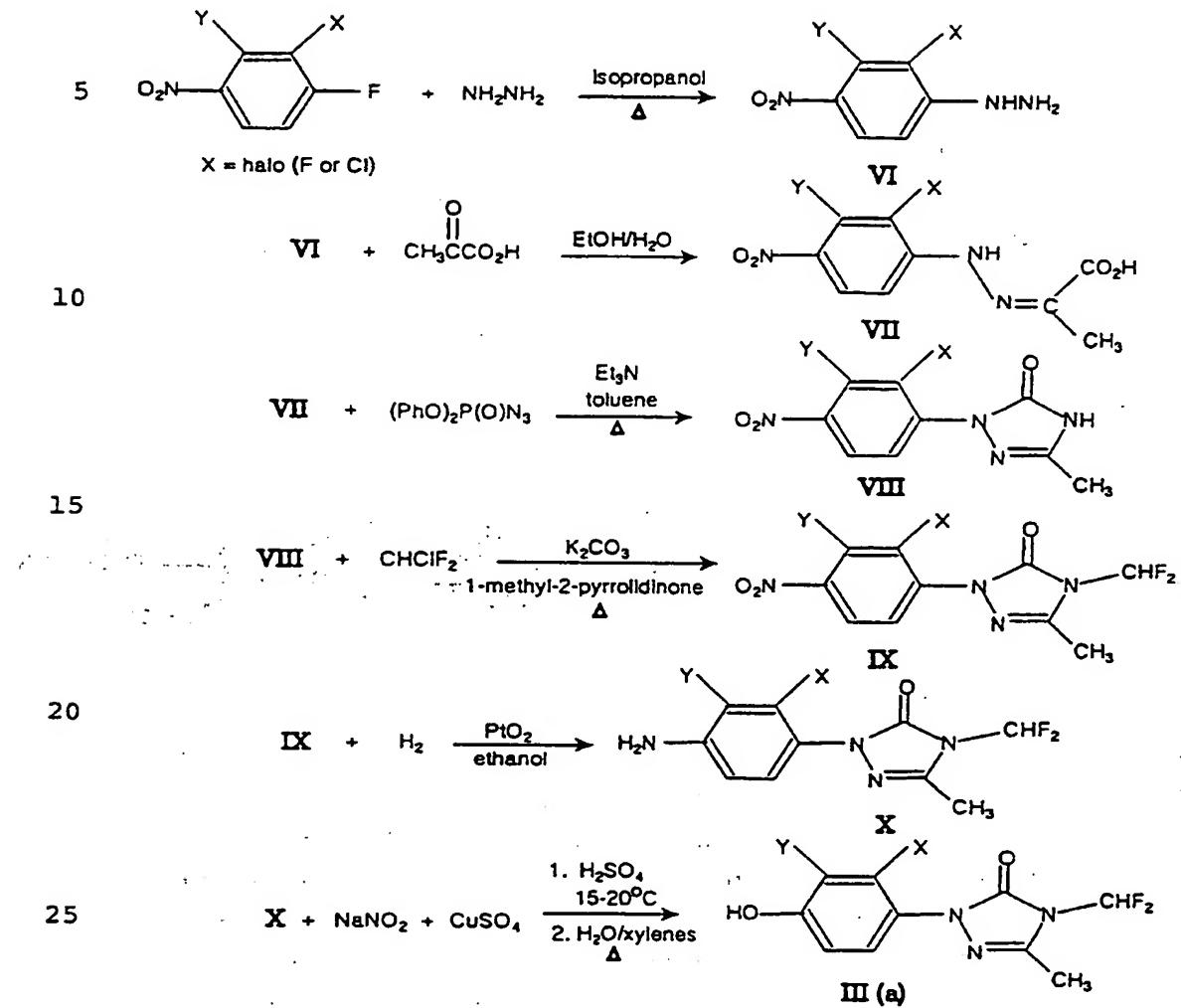
SCHEMA A



Thus, a mixture of an appropriately substituted formyl-substituted phenol and a methyl 2-bromoalkanoate was heated at 70°C in 2-butanone in the presence of potassium carbonate. Usually the reaction was run overnight, producing the corresponding 2-(substituted formylphenoxy)alkanoate (IV). This compound was then reduced with sodium methoxide and sodium borohydride in methanol, yielding the corresponding 2-(hydroxymethyl-phenoxy)alkanoate (V). Reaction of V with thionyl chloride in methylene chloride in the presence of a catalytic amount of pyridine produced the corresponding 2-(chloromethylphenoxy)alkanoate (II).

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SCHEMA B



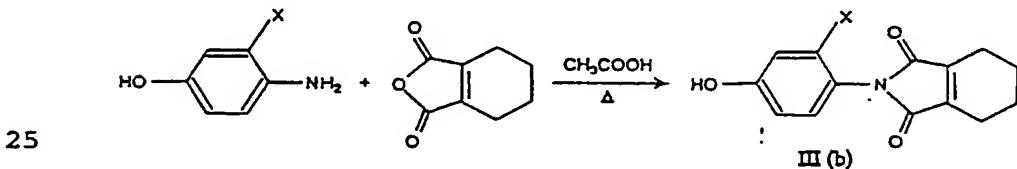
30 To prepare compounds of the invention in which Q is 4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl, a 3-halo-4-fluoronitrobenzene was reacted with hydrazine in isopropanol at reflux, preparing the corresponding 2-halo-4-nitrophenylhydrazine
 35 (VI). Reaction of VI with pyruvic acid in ethanol and

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water produced the 2-halo-4-nitrophenylhydrazone of pyruvic acid (VII). Preparation of the triazolinone ring was accomplished by heating VII with diphenyl-phosphoryl azide and triethylamine in toluene at 5 reflux, producing 1-(2-halo-4-nitrophenyl)-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one (VIII). Chlorodifluoromethane was then reacted with VIII and potassium carbonate in 1-methyl-2-pyrrolidinone by heating the mixture at 120°C, producing 1-(2-halo-4-nitrophenyl)-4-10 difluoromethyl-3-methyl-1,2,4-triazol-5(1H)-one (IX). Hydrogenation of IX in ethanol using platinum oxide as catalyst produced 1-(4-amino-2-halophenyl)-4,5-dihydro-4-difluoromethyl-3-methyl-1,2,4-triazol-5(1H)-one (X). Preparation of intermediate III (a) was completed by 15 reaction of X with sodium nitrite in sulfuric acid and subsequently with copper (II) sulfate in the presence of iron (II) sulfate in a mixture of water and xylenes.

SCHEMA C

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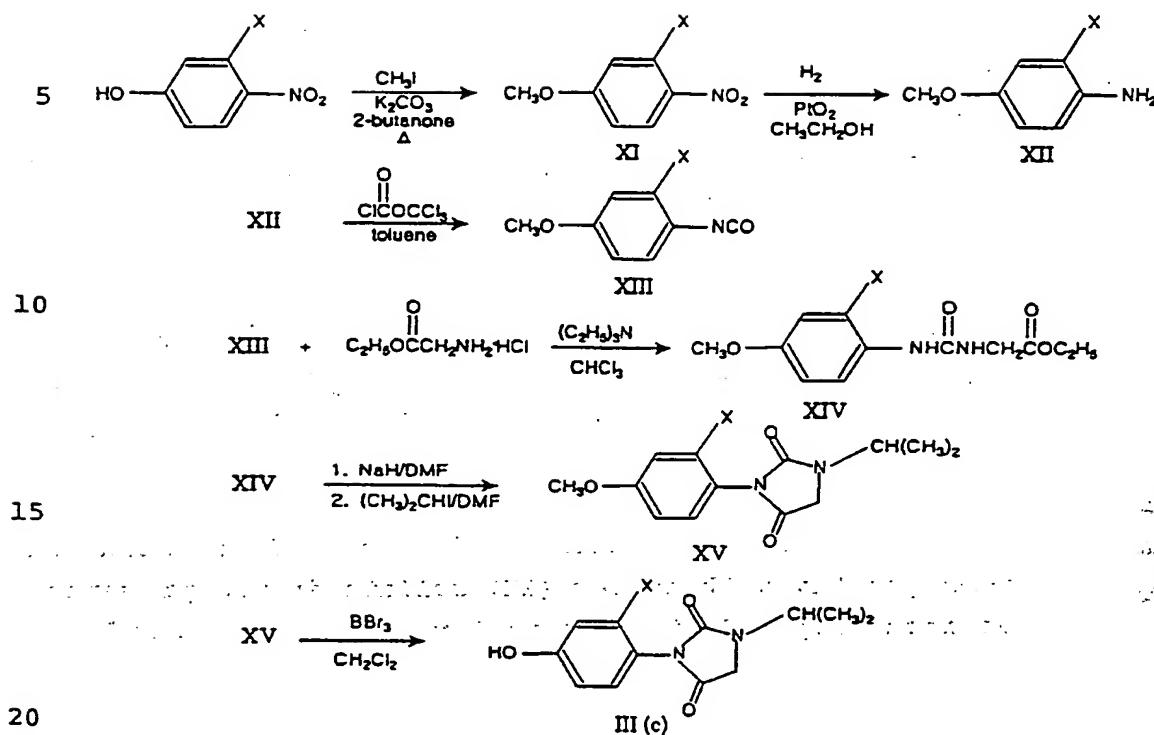


To prepare the tetrahydronaphthalimide-substituted intermediate (III(b)), an appropriately substituted 4-30 aminophenol was refluxed with tetrahydronaphthalic anhydride, producing the corresponding N-(4-hydroxy-substituted-phenyl)tetrahydronaphthalimide.

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SCHEMA D



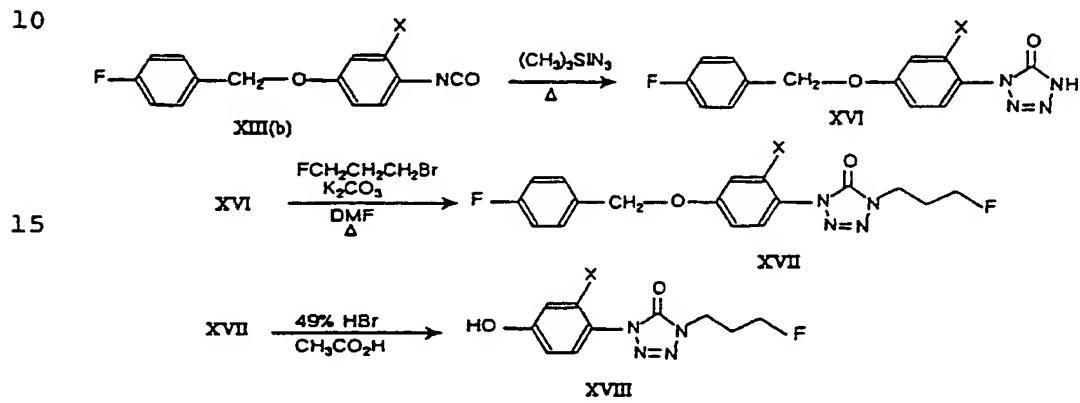
An appropriately substituted 4-nitrophenol was heated with methyl iodide in the presence of potassium carbonate in 2-butanone to prepare the corresponding substituted 4-nitroanisole (XI). Compound XI was hydrogenated over platinum oxide, producing a substituted 4-methoxyaniline (XII). The reaction of XII with trichloromethyl chloroformate prepared the corresponding substituted 4-methoxyphenyl isocyanate (XIII). Reaction of this isocyanate with the ethyl ester of glycine hydrochloride and triethylamine in chloroform yielded N-(4-methoxy-substituted-phenyl)-N'-ethoxy-

- 10 -

carbonylmethylurea (XIV). Sequentially, XIV was reacted with sodium hydride and then with 2-iodo-propane, yielding ultimately 1-(1-methylethyl)-3-(4-methoxy-substituted-phenyl)imidazolidin-2,4-dione (XV).

5 Cleavage of the methoxy group of XV with boron tribromide yielded intermediate III (c).

SCHEMA E

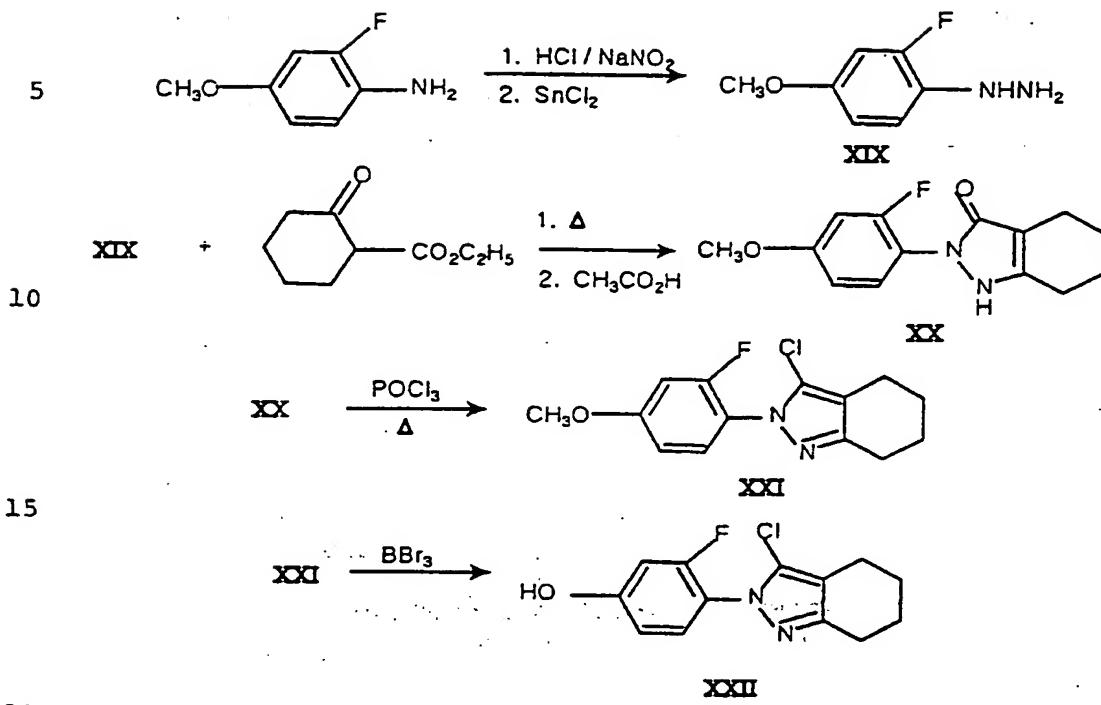


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An appropriately substituted phenyl isocyanate (XIII(b)) was prepared by the first three steps of Schema D and then was reacted with trimethylsilyl azide to prepare the correspondingly substituted phenyl-substituted tetrazolinone (XVI). After this tetra-zolinone was alkylated in the 4-position with 1-bromo-3-fluoropropane to make the 3-fluoropropyl-substituted compound (XVII), the 4-fluorobenzyl protecting group was removed with 49% hydrobromic acid in acetic acid, yielding the desired hydroxy-substituted intermediate (XVIII).

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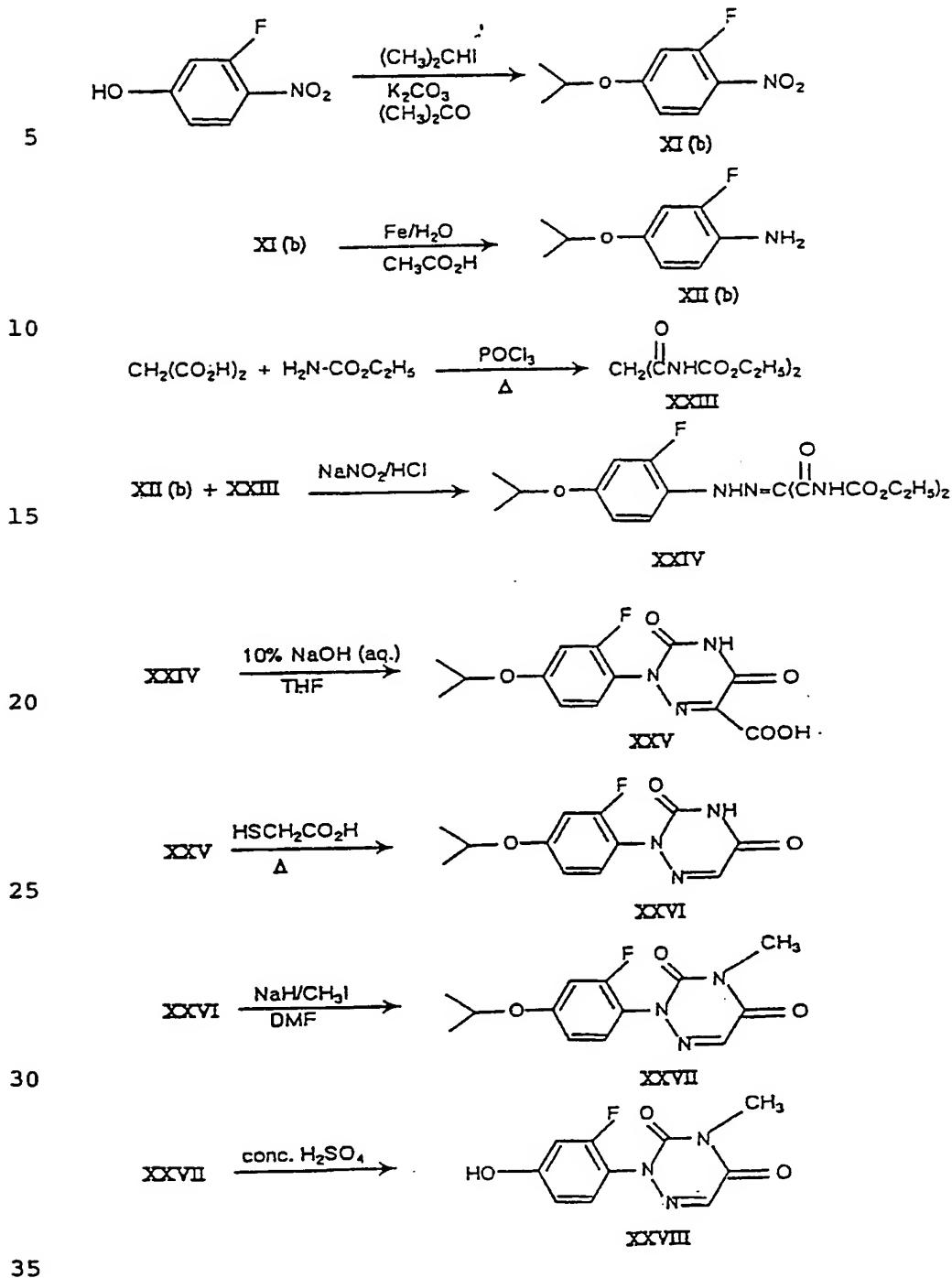
SCHEMA F



The diazonium salt of 2-fluoro-4-methoxyaniline was prepared using sodium nitrite and hydrochloric acid and was then reduced *in situ* with tin(II) chloride to prepare the correspondingly substituted phenylhydrazine (XIX). Reaction of this hydrazine with ethyl 2-cyclohexanonecarboxylate and subsequent heating of the product in the presence of acetic acid produced a mixture of 2-(2-fluoro-4-methoxyphenyl)-4,5,6,7-tetrahydro-1H-indazol-3-one (XX) and the 2-fluoro-4-methoxyphenylhydrazone of 2-cyclohexanonecarboxylic acid. This mixture was heated in phosphorus oxychloride, yielding 3-chloro-2-(2-fluoro-4-methoxyphenyl)-4,5,6,7-tetrahydroindazole (XXI), which was then cleaved with boron tribromide to the desired 3-chloro-2-(2-fluoro-4-hydroxyphenyl)-4,5,6,7-tetrahydroindazole (XXII).

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SCHEMA G



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Etherification of 3-fluoro-4-nitrophenol with iso-propyl iodide in the presence of potassium carbonate produced 2-fluoro-4-isopropoxynitrobenzene (XI(b)), which was reduced to 2-fluoro-4-isopropoxyaniline
5 (XII(b)) with iron in aqueous acetic acid. Malonic acid was reacted with urethane (ethyl carbamate) in phosphorus oxychloride to produce malonyldiurethane (XXIII). The reaction of XII(b) and XXIII was effected by sodium nitrite and hydrochloric acid, producing 2-
10 (4-isopropoxy-2-fluorophenyl)hydrazonomalonyldiurethane (XXIV), which was cyclized with sodium hydroxide to the corresponding 2-(substituted phenyl)-1,2,4-triazine-3,5-dion-6-carboxylic acid (XXV). Decarboxylation of XXV with thioglycolic acid and heat yielded XXVI which
15 was then methylated at the 4-position with sodium hydride and methyl iodide producing the corresponding 2-(substituted phenyl)-4-methyl-1,2,4-triazine-3,5-dione (XXVII). In the final step the isopropyl protecting group was cleaved from the molecule with concentrated sulfuric acid, producing the desired hydroxy-
20 substituted intermediate (XXVIII).

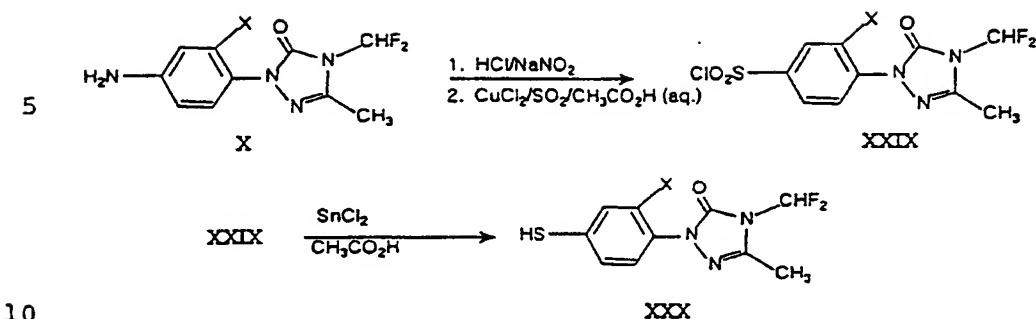
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SCHEMA H



Preparation of the mercapto analog of intermediate III(a) started with intermediate X, which was converted to the corresponding diazonium salt. This diazonium compound was immediately reacted with copper (II) chloride and sulfur dioxide in aqueous acetic acid, producing the corresponding substituted phenylsulfonyl chloride (XXIX). Reduction of the sulfonyl chloride moiety to a thiol group was effected using tin (II) chloride in acetic acid, yielding, for example, 4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorothiophenol (XXX), the desired intermediate.

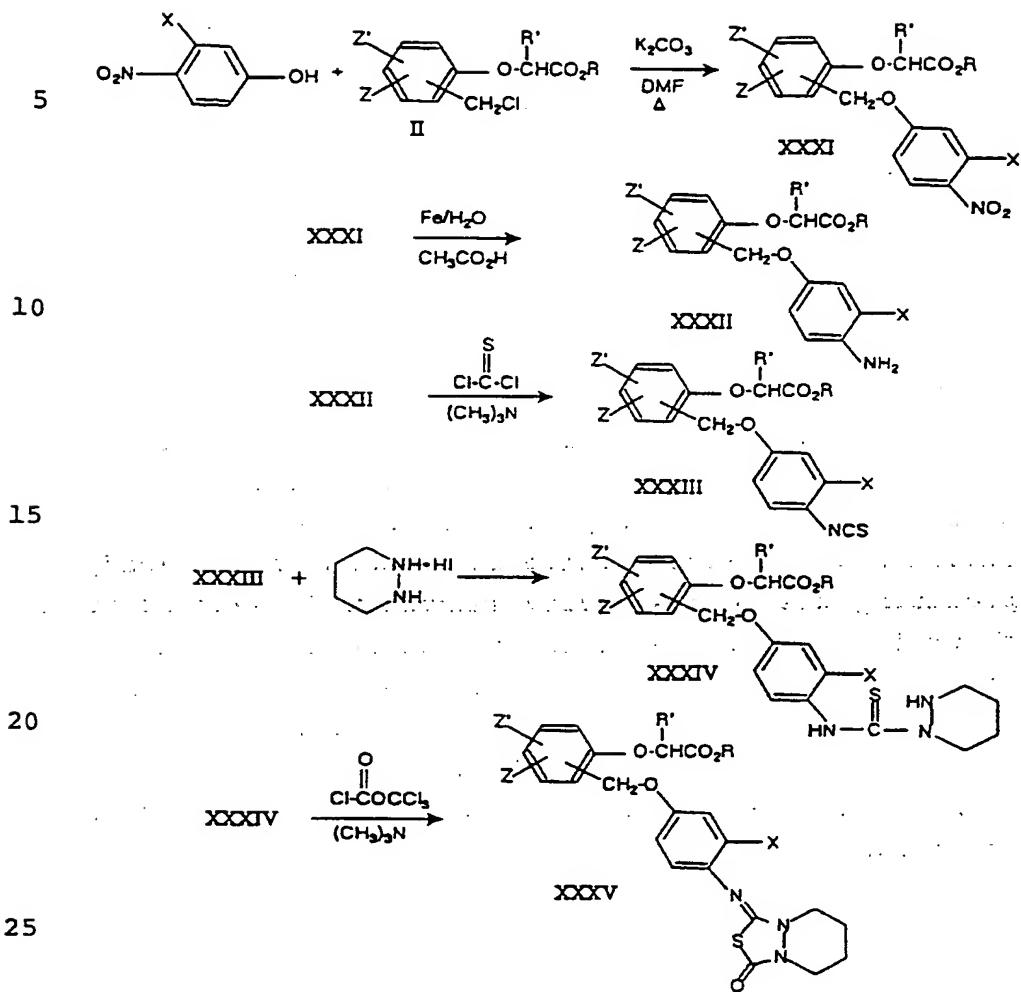
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- 15 -

SCHEMA I



Unlike the preparation of the other heterocyclic-substituted herbicidal compounds of this invention, where the final step is the reaction of II and III to form the herbicide, in the preparation of the compounds in which Q is 8-thia-1,6-diazabicyclo[4.3.0]nonane-7-on-9-ylimino II and III are first reacted to form an intermediate prior to forming the heterocycle. Thus, II was reacted with 3-fluoro-4-nitrophenol in N,N-di

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methylformamide in the presence of potassium carbonate, yielding a 2-(4-nitrophenoxy)methylphenoxy)alkanoate (XXXI). Reduction of XXXI with iron and water in acetic acid produced the corresponding amino compound

5 (XXXII), which was then converted to the isothiocyanate (XXXIII) with thiophosgene and trimethylamine. Perhydropyridazine monohydroiodide and XXXIII were then reacted, forming a 2-(4-perhydropyridazin-1-ylthio-carbonylaminophenoxy)methylphenoxy)alkanoate (XXXIV).

10 Cyclization of XXXIV using trichloromethyl chloroformate and triethylamine yielded, for example, methyl 2-[2-[4-(8-thia-1,6-diazabicyclo[4.3.0]nonane-7-on-9-ylimino)-3-fluorophenoxy)methyl]-5-methylphenoxy]propionate (XXXV), the desired herbicidal compound.

15 Similarly, the compounds in which Q is 1-methyl-6-trifluoromethyl-2,4-pyrimidinedione-3-yl may be prepared by the method of Schema I through the preparation of XXXII. Then XXXII is converted to the isocyanate with phosgene in place of thiophosgene, and the iso-

20 cyanate is reacted with ethyl 3-amino-4,4,4-trifluoro-2-butenoate to yield the desired herbicidal compound.

25 In this specification "lower alkyl" contains 1 to 6 carbons, preferably 1 to 4, "lower alkenyl" or "lower alkynyl" contains 2 to 6 carbons, preferably 2 to 4, "cycloalkyl" contains 3 to 6 carbons, and "halogen" or "halo" means bromine, chlorine, or fluorine, preferably chlorine or fluorine.

30 The methods for preparing the novel herbicidal compounds of the invention are exemplified below.

All NMR spectra are reported as proton assignments in ppm in CDCl₃.

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EXAMPLE 1

METHYL 2-[2-[4-(4-DIFLUOROMETHYL-4,5-DIHYDRO-3-METHYL-1,2,4-TRIAZOL-5(1H)-ON-1-YL)-3-FLUOROPHENOXY-METHYL]-5-METHYLPHENOXY]PROPIONATE

5 (Compound 12)

Step A: 2-Fluoro-4-nitrophenylhydrazone of pyruvic acid

A thick mixture of 21.6 g (0.126 mole) of wet 2-fluoro-4-nitrophenylhydrazine in 100 mL of ethanol and 11.27 g (0.128 mole) of pyruvic acid in 20 mL of water were mixed. After the reaction mixture had stirred for 20 minutes, it was filtered to yield 15.5 g of a yellow solid, m.p. 210°C (decomposition). An NMR spectrum of the product was consistent with the structure of the 2-fluoro-4-nitrophenylhydrazone of pyruvic acid. This reaction was repeated to obtain additional product.

Step B: 1-(2-Fluoro-4-nitrophenyl)-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one

A mixture of 29.62 g (0.123 mole) of the 2-fluoro-4-nitrophenylhydrazone of pyruvic acid, 12.45 g (0.123 mole) of triethylamine, and 33.85 g (0.123 mole) of diphenylphosphoryl azide in 200 mL of toluene was heated slowly to reflux. Heating at reflux was continued for two hours during which this yellow mixture became an orange solution. After cooling to room temperature, the reaction mixture was extracted with a solution of 17.0 g (0.425 mole) of sodium hydroxide in 200 mL of water. The aqueous extract was separated and was almost completely neutralized with concentrated hydrochloric acid. Just before pH 7 was reached, dry ice was added to the solution, completing the neutralization and causing a brown solid to precipitate. Filtration of this mixture yielded 26.15 g of 1-(2-fluoro-4-nitrophenyl)-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one as a brown solid, m.p. 211-212°C. The NMR spectrum was consistent with the proposed

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structure.

Step C: 1-(2-Fluoro-4-nitrophenyl)-4-difluoromethyl-
4,5-dihydro-1,2,4-triazol-5(1H)-one

A mixture of 5.0 g (0.025 mole) of 1-(2-fluoro-4-nitrophenyl)-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one and 29.0 g (0.210 mole) of dry, ground potassium carbonate in 200 mL of 1-methyl-2-pyrrolidinone was heated at 120°C for 30 minutes. Chlorodifluoromethane was bubbled into the reaction mixture for five minutes.

Thin layer chromatography of the reaction mixture revealed that the reaction had not gone to completion. Therefore, chlorodifluoromethane was bubbled into the reaction mixture for an additional three minutes. The reaction mixture was poured over ice and then was neutralized with concentrated hydrochloric acid. This mixture was extracted twice with diethyl ether. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under reduced pressure, leaving a dark brown solid residue. This solid was dissolved in 100 mL of acetic acid and 5 mL of hydrobromic acid, and this solution was heated at reflux for one hour. This mixture was poured over ice and was then extracted with ethyl acetate. This extract was washed twice with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under reduced pressure, leaving a black oil as a residue. This residue was put on a silica gel column and eluted with methylene chloride/ethyl acetate (97.5/2.5). After the product-containing fractions had been combined, the solvents were evaporated under reduced pressure, leaving 4.6 g of 1-(2-fluoro-4-nitrophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one as a residue, m.p. 72-77°C. The NMR spectrum was consistent with the proposed structure.

This reaction was repeated to obtain additional 1-

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(2-fluoro-4-nitrophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one for the remainder of the synthesis.

Step D: 1-(2-Fluoro-4-aminophenyl)-4-difluoromethyl-
5 4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one

A mixture of 24.5 g (0.085 mole) of 1-(2-fluoro-4-nitrophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one and 0.30 g of platinum oxide in 250 mL of absolute ethanol was hydrogenated in a Parr
10 hydrogenation apparatus. The calculated amount of hydrogen required was taken up in 45 minutes. The reaction mixture was filtered through a Buchner funnel, and the filtrate was evaporated under reduced pressure, leaving a dark brown solid residue. This residue was
15 placed on a silica gel column and eluted with methylene chloride/ethyl acetate (75/25). After the product-containing fractions were combined, evaporation of the solvents under reduced pressure yielded 20.1 g of 1-(2-fluoro-4-aminophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one. The NMR spectrum was
20 consistent with the proposed structure.

Step E: 1-(2-Fluoro-4-hydroxyphenyl)-4-difluoromethyl-
4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one

A solution of 20.0 g (0.0774 mole) of 1-(2-fluoro-4-aminophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one in 100 mL of concentrated sulfuric acid was cooled to 15-20°C. A solution of 5.3 g (0.0774 mole) of sodium nitrite in 20 mL of water was added slowly to the sulfuric acid solution while the
25 temperature was maintained between 15°C and 20°C. The dark orange solution was stirred for an hour at this temperature. The solution was then added rapidly to a solution of 250 g (1.00 mole) of copper (II) sulfate pentahydrate and 2.0 g (0.0072 mole) of iron (II) sulfate heptahydrate in 250 mL of water and 250 mL of mixed xylenes. This two-phase solution was heated at
30
35

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reflux for one hour, after which it was cooled and the phases separated. The organic layer was dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated under reduced pressure, leaving a brown oil. The aqueous layer was extracted with ethyl acetate, and the extract was dried over anhydrous magnesium sulfate and then filtered. The extract was combined with the brown oil from the organic phase, and the solvent was evaporated under reduced pressure, again leaving a brown oil. This brown oil was placed on a silica gel column and eluted with methylene chloride/ethyl acetate (90/10). The product-containing fractions were combined, and the solvent was evaporated under reduced pressure, leaving 12.17 g of 1-(2-fluoro-4-hydroxyphenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one, m.p. 112-114°C. The NMR spectrum was consistent with the proposed structure.

Step F: Methyl 2-(formyl-5-methylphenoxy)propionate

A mixture of 6.0 g (0.0441 mole) of 4-methylsalicylaldehyde, 7.31 g (0.0529 mole) of potassium carbonate, and 8.62 g (0.0529 mole) of methyl 2-bromopropionate in 50 mL of 2-butanone was heated at 70°C for approximately seventeen hours. The mixture was then filtered, and the filtrate was evaporated under reduced pressure, leaving a light yellow oil as a residue. This oil was placed on a silica gel column and eluted first with diethyl ether/petroleum ether (25/75) and then with diethyl ether. After the product-containing fractions were combined and the solvents evaporated under reduced pressure, 8.2 g of methyl 2-(2-formyl-5-methylphenoxy)propionate was recovered as a white solid, m.p. 65-68°C. The NMR and IR spectra were consistent with the proposed structure.

Step G: Methyl 2-(2-hydroxymethyl-5-methylphenoxy)-propionate

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To a solution of 7.89 g (0.0355 mole) of methyl 2-(2-formyl-5-methylphenoxy)propionate in 20 mL of methanol, cooled to 5°C, was added a solution of 0.10 g (0.0018 mole) of sodium methoxide in 20 mL of methanol.

5 While the temperature was maintained between 0°C and 5°C, 0.36 g (0.0094 mole) of sodium borohydride was added to the reaction during a period of about 10 minutes. The reaction mixture was allowed to warm to ambient temperature, where it was stirred for two

10 hours. At the end of this period, the reaction mixture was poured into 75 mL of 0.25 N hydrochloric acid. This mixture was extracted twice with methylene chloride. The combined extracts were washed with a saturated aqueous solution of sodium chloride, dried

15 over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under reduced pressure, leaving a colorless oil as a residue. This oil was placed on a silica gel column and eluted first with methylene chloride/ethyl acetate (95/5) and then with the same

20 solvents (90/10). After the product-containing fractions were combined and the solvents evaporated under reduced pressure, 5.76 g of methyl 2-(2-hydroxy-methyl-5-methylphenoxy)propionate was isolated as a colorless oil. The NMR and IR spectra were consistent

25 with the proposed structure.

Step H: Methyl 2-(2-chloromethyl-5-methylphenoxy)-propionate

A solution of 2.20 g (0.0098 mole) of methyl 2-(2-hydroxymethyl-5-methylphenoxy)propionate in 10 mL of dry methylene chloride was added to a colorless solution of 1.28 g (0.0108 mole) of thionyl chloride and 5 drops of pyridine in 10 mL of dry methylene chloride during a 10 minute period. This mixture was heated at reflux for one hour and then poured into 50 mL of water. The phases were separated, and the aqueous phase was extracted three times with methylene

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chloride. These extracts were combined with the organic phase, which was then washed three times with a saturated aqueous solution of sodium bicarbonate and once with a saturated aqueous solution of sodium chloride. The organic phase was then dried over anhydrous magnesium sulfate, filtered, and the filtrate was evaporated under reduced pressure, leaving a yellow oil as a residue. This oil was placed on a silica gel column and eluted with methylene chloride. After the product-containing fractions were combined and the solvent evaporated under reduced pressure, 2.06 g of methyl 2-(2-chloromethyl-5-methylphenoxy)propionate was recovered as a colorless oil. The NMR spectrum was consistent with the proposed structure.

Step I: Methyl 2-[2-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate

A mixture of 0.50 g (0.0019 mole) of 1-(2-fluoro-4-hydroxyphenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one, 0.39 g (0.0028 mole) of anhydrous potassium carbonate, and 0.92 g (0.0038 mole) of methyl 2-(2-chloromethyl-5-methylphenoxy)propionate in 20 mL of N,N-dimethylformamide was heated at 90°C for approximately 17 hours. At the end of this period the mixture was poured over ice, and the resulting mixture was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under reduced pressure, leaving an orange oil as a residue. This oil was placed on a silica gel column and eluted first with methylene chloride and then with methylene chloride/ethyl acetate (97.5/2.5). After the product-containing fractions were combined and the solvents evaporated under reduced pressure, 0.82 g of 2-[2-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-

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triazol-5(1H)-on-1-yl)-3-fluorophenoxy]propionate was recovered as a yellow oil. The NMR and IR spectra were consistent with the proposed structure. NMR: 1.60 (d, 3H, J_{HH} = 8.0 Hz); 2.30 (s, 5 3H); 2.44 (s, 3H); 3.76 (s, 3H); 4.84 (q, 1H, J_{HH} = 8.0 Hz); 5.16 (dd, 2H, J_{HH} = 10.0 Hz); 6.56 (s, 1H); 6.78-7.32 (m, 6H).

EXAMPLE 2

METHYL 2-[2-[3-FLUORO-4-(3,4,5,6-TETRAHYDRO-1-PHTHALIMIDYL)PHENOXYMETHYL]-5-CHLOROPHOXY]PROPIONATE
10 (Compound 27)

Step A: Synthesis of 4-amino-3-fluorophenol

To a mixture of 10.0 g (0.0640 mole) of 3-fluoro-4-nitrophenol in 100 mL of acetic acid and 10 mL of water 15 heated to 50°C was added 10.0 g (0.179 mole) of iron powder in small portions during a 35 minute period. The stirred reaction mixture was heated at 50°C for an additional three hours, after which it was cooled and filtered. The filtrate was used in Step B without 20 further purification.

Step B: N-(2-fluoro-4-hydroxyphenyl)-3,4,5,6-tetrahydrophthalimide

The filtrate from Step A was mixed with 9.74 g (0.0640 mole) of 3,4,5,6-tetrahydronaphthalic anhydride, 25 and the mixture was heated at reflux for approximately 64 hours. At the end of this period, the dark brown solution was poured over ice and extracted in succession with ethyl acetate and diethyl ether. The extracts were combined, washed with water, dried over 30 anhydrous magnesium sulfate, and filtered. The solvents were evaporated under reduced pressure from the filtrate, leaving a dark brown oil as residue. This was placed on a silica gel column and eluted with methylene chloride/ethyl acetate (95/5). After the 35 product-containing fractions were combined and the solvents evaporated under reduced pressure, 14.71 g of

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N-(2-fluoro-4-hydroxyphenyl)-3,4,5,6-tetrahydropthalimide was recovered as an orange solid, m.p. 132-136°C. The NMR spectrum was consistent with the proposed structure.

5 Step C: Methyl 2-(5-chloro-2-formylphenoxy)propionate

A mixture of 22.0 g (0.141 mole) of 4-chlorosalicylaldehyde, 30 g (0.22 mole) of anhydrous potassium carbonate, and 30.0 g (0.184 mole) of methyl 2-bromo-propionate in 120 mL of N,N-dimethylformamide was

10 heated at 80°C for approximately 17 hours. At the end of that period, the reaction mixture was poured over ice and extracted successively with diethyl ether and ethyl acetate. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and 15 filtered. The solvents were then evaporated under reduced pressure, leaving a residue weighing 20 g.

This residue was purified by placing it on a silica gel column and eluting with diethyl ether/petroleum ether (25/75). After the product-containing fractions were 20 combined and the solvents evaporated under reduced pressure, 6.23 g of methyl 2-(5-chloro-2-formylphenoxy)propionate was isolated as a yellow liquid.

Similarly, other fractions were combined and evaporated, yielding 1.69 g of methyl 2-(3-chloro-2-formylphenoxy)propionate as a yellow liquid. The NMR spectra of both compounds were consistent with proposed 25 structure of each. This reaction was repeated several times.

Step D: Methyl 2-(5-chloro-2-hydroxymethylphenoxy)-
30 propionate

To a solution of 0.10 g (0.018 mole) of sodium methoxide in 20 mL of methanol that had been cooled to 5°C was added a solution of 8.0 g of methyl 2-(5-chloro-2-formylphenoxy)propionate in 20 mL of methanol. 35 While the temperature was maintained between 0°C and 5°C, to this mixture was added 0.50 g (0.013 mole) of

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sodium borohydride. This addition required 10 minutes, during which gas was evolved. The yellow solution was allowed to warm up to room temperature, where it was stirred for four hours. At the end of this period the
5 reaction mixture was poured into 100 mL of 0.25 N hydrochloric acid. This mixture was extracted with methylene chloride. The extract was washed with a saturated aqueous solution of sodium chloride, dried over anhydrous magnesium sulfate, and filtered. The
10 filtrate was evaporated under reduced pressure, leaving a yellow oil as a residue. This oil was placed on a silica gel column and eluted with methylene chloride/-ethyl acetate (95/5). After the product-containing fractions were combined and the solvents evaporated
15 under reduced pressure, 4.42 g of methyl 2-(5-chloro-2-hydroxymethylphenoxy)propionate was isolated as an orange oil, which subsequently solidified, m.p. 51-52°C.

Step E: Methyl 2-(2-chloromethyl-5-chlorophenoxy)-
20 propionate

By the method of Example 1, Step H, 1.0 g (0.0038 mole) of methyl 2-(5-chloro-2-hydroxymethylphenoxy)-propionate and 0.5 g (0.0042 mole) of thionyl chloride were reacted in 20 mL of methylene chloride. After
25 purification, 0.88 g of methyl 2-(2-chloromethyl-5-chlorophenoxy)propionate was isolated as a yellow liquid. The NMR spectrum was consistent with the proposed structure.

Step F: Methyl 2-[2-[3-fluoro-4-(3,4,5,6-tetrahydro-1-phthalimidyl)phenoxy]methyl]-5-chlorophenoxy)-
30 propionate

By the method of Example 1, Step I, 0.50 g (0.0019 mole) of N-(2-fluoro-4-hydroxyphenyl)-3,4,5,6-tetrahydrophthalimide, 0.88 g (0.0034 mole) of methyl 2-(2-chloromethyl-5-chlorophenoxy)propionate, and 0.39 g (0.0028 mole) of potassium carbonate were reacted in 20

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mL of 2-butanone. After purification, 0.58 g of methyl 2-[2-[3-fluoro-4-(3,4,5,6-tetrahydro-1-phthalimidyl)-phenoxy]methyl]-5-chlorophenoxy]propionate was isolated as a yellow solid, m.p. 110-112°C. The NMR and IR spectra were consistent with the proposed structure.

NMR: 1.64 (d, 3H, $J_{HH} = 8$ Hz); 1.80 (bs, 4H); 2.40 (bs, 4H); 3.78 (s, 3H); 4.84 (q, 1H, $J_{HH} = 8.0$ Hz); 5.14 (s, 2H); 6.78-7.38 (m, 6H).

EXAMPLE 3

10 METHYL 2-[2-[3-FLUORO-4-[1-(1-METHYLETHYL)-IMIDAZOL-
IDIN-2,4-DION-3-YL]PHENOXYMETHYL]-5-CHLOROPHENOXY]-
PROPIONATE
(Compound 44)

Step A: 2-Fluoro-4-methoxyphenyl isocyanate

To a solution of 13.75 g (0.0967 mole) of 2-fluoro-4-methoxyaniline in 120 mL of toluene was slowly added over a period of 30 minutes a solution of 19.13 g (0.0967 mole) of trichloromethyl chloroformate in 30 mL of toluene. During the addition the temperature rose to 35°C. The reaction mixture was stirred without external heating for 30 minutes and then heated at reflux for approximately 17 hours. At the end of this time all of the solvent was removed by distillation, leaving 2-fluoro-4-methoxyphenyl isocyanate as a purple liquid, which was used immediately in Step B.

Step B: N-(2-Fluoro-4-methoxyphenyl)-N'-ethoxycarbonylmethylurea

A solution of 2-fluoro-4-methoxyphenyl isocyanate (assumed to weigh 16.2 g (0.0967 mole) from Step A), 30 13.50 g (0.0967 mole) of glycine ethyl ester hydrochloride in 100 mL of chloroform was placed in a flask, and a solution of 9.28 g (0.0967 mole) of triethylamine in 25 mL of chloroform was added during a 20 minute period. The temperature rose to 38°C during the 35 addition. Upon completion of addition, the reaction mixture was stirred at ambient temperature for three

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hours and then poured into a mixture of heptane and water. By filtration, N-(2-fluoro-4-methoxyphenyl)-N'-ethoxycarbonylmethylurea was isolated from this mixture as a purple solid, m.p. 158-159°C. The organic
5 phase of the filtrate was separated, dried over anhydrous magnesium sulfate, and filtered. The solvent was evaporated from the filtrate under reduced pressure, leaving a purple solid as residue. This solid was recrystallized from ethyl acetate/petroleum
10 ether. The recrystallized solid was placed on a silica gel column and eluted sequentially with methylene chloride, methylene chloride/ethyl acetate (90/10), and finally methylene chloride/ethyl acetate (75/25). After the product-containing fractions were combined
15 and the solvents evaporated under reduced pressure, additional N-(2-fluoro-4-methoxyphenyl)-N'-ethoxycarbonylmethylurea was isolated as a purple solid, m.p. 158-159°C. The total yield of N-(2-fluoro-4-methoxyphenyl)-N'-ethoxycarbonylmethylurea weighed 17.33 g.
20 The NMR spectra of these solids were consistent with the proposed structure.

Step C: 1-(1-Methylethyl)-3-(2-fluoro-4-methoxyphenyl)imidazolidin-2,4-dione
A solution of 17.02 g (0.0630 mole) of N-(2-fluoro-4-methoxyphenyl)-N'-ethoxycarbonylmethylurea in 50 mL of
25 N,N-dimethylformamide was added dropwise to a suspension of 2.65 g (0.0662 mole) of sodium hydride in 30 mL of N,N-dimethylformamide during a 20 minute period. Gas evolution and a slight rise in temperature
30 occurred during the addition. This mixture was stirred at room temperature for 45 minutes, by which time it had become a homogeneous solution. To this solution was added dropwise, over a period of 15 minutes, a solution of 21.42 g (0.126 mole) of 2-iodopropane in 10
35 mL of N,N-dimethylformamide. The temperature rose to 38°C during the addition period. This reaction mixture

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was stirred for approximately 65 hours, then poured over ice and extracted with diethyl ether. The extract was washed twice with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was
5 evaporated under reduced pressure, leaving an orange oil as a residue. This oil was placed on a silica gel column and eluted sequentially with 97.5/2.5 and 95/5 mixtures of methylene chloride and ethyl acetate.
After the product-containing fractions were combined
10 and the solvents evaporated under reduced pressure, 5.85 g of 1-(1-methylethyl)-3-(2-fluoro-4-methoxy-phenyl)imidazolidin-2,4-dione was isolated as an orange solid, m.p. 88-90°C.
Step D: 1-(1-methylethyl)-3-(2-fluoro-4-hydroxy-phenyl)imidazolidin-2,4-dione
15 A 1 M methylene chloride solution of boron tribromide (41.6 ml, 0.0416 mole) was cooled to -20°C. While this temperature was maintained, a solution of 5.55 g (0.0208 mole) of 1-(1-methylethyl)-3-(2-fluoro-
20 4-methoxyphenyl)imidazolidin-2,4-dione in 25 mL of methylene chloride was added to the reaction during an eight minute period. The reaction mixture was allowed to warm to room temperature, where it was stirred for approximately 17 hours. At the end of this time the
25 reaction was poured over ice, and the resulting two-phase mixture was filtered. The organic phase was separated, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under reduced pressure, leaving a black solid as a residue. This
30 solid was recrystallized from ethyl acetate/petroleum ether, to yield 3.25 g of 1-(1-methylethyl)-3-(2-fluoro-4-hydroxyphenyl)imidazolidin-2,4-dione as a tan solid, m.p. 190-192°C. The NMR and IR spectra were consistent with the proposed structure.
35 Step E: Methyl 2-[2-[3-fluoro-4-[1-(1-methylethyl)-imidazolidin-2,4-dion-3-yl]phenoxy]methyl]-5-

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chlorophenoxy]propionate

By the method of Example 1, Step I, 0.60 g (0.0024 mole) of 1-(1-methylethyl)-3-(2-fluoro-4-hydroxy-phenyl)imidazolidin-2,4-dione, 1.24 g (0.0048 mole) of 5 methyl 2-(2-chloromethyl-5-chlorophenoxy)propionate (Example 2, Step E), and 0.5 g (0.0036 mole) of potassium carbonate were reacted in 25 mL of 2-butanone. After purification, 1.04 g of methyl 2-[2-[3-fluoro-4[1-(1-methylethyl)imidazolidin-2,4-dion-3-yl]phenoxy]methyl]-5-chlorophenoxy]propionate was 10 isolated as a yellow oil. The NMR and IR spectra were consistent with the proposed structure. NMR: 1.24 (d, 6H, $J_{HH} = 8$ Hz); 1.64 (d, 3H, $J_{HH} = 8$ Hz); 3.68 (s, 3H); 3.96 (s, 1H); 4.44 (septet, 1H, $J_{HH} = 8.0$ Hz); 15 5.04 (q, 1H, $J_{HH} = 8.0$ Hz); 5.24 (s, 2H); 6.80-7.34 (m, 5H).

EXAMPLE 4

METHYL 2-[2-[4-[1,4-DIHYDRO-4-(3-FLUOROPROPYL)-5H-TETRAZOL-5-ON-1-YL]-3-FLUOROPHOXYMETHYL]-5-METHYL-20 PHENOXY]PROPIONATE

(Compound 64)

Step A: 4-Fluorophenylmethyl 3-fluoro-4-nitrophenyl ether

A stirred mixture of 10.0 g (0.063 mole) of 3-fluoro-4-nitrophenol, 17.0 g (0.090 mole) of 4-fluorophenylmethyl chloride, and 12.42 g (0.090 mole) of 25 anhydrous potassium carbonate in 80 mL of methyl ethyl ketone was heated at 70°C for approximately 17 hours. The reaction mixture was then cooled and filtered and 30 the filtrate evaporated under reduced pressure, leaving 13.10 g of 4-fluorophenylmethyl 3-fluoro-4-nitrophenyl ether as a solid; m.p. 90-91°C.

Step B: 4-Fluorophenylmethyl 4-amino-3-fluorophenyl ether

35 A solution of 11.0 g (0.041 mole) of 4-fluorophenylmethyl 3-fluoro-4-nitrophenyl ether in 100 mL of

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glacial acetic acid and 10 mL of water was heated to 50°C. To this hot solution was added 10.0 g (0.18 mole) of powdered iron. The reaction mixture was allowed to cool to ambient temperature, where it 5 stirred for an additional hour. The reaction mixture was filtered through a bed of Celite® filter aid, and the Celite bed was washed in succession with ethyl acetate and 200 mL of water. The washes and the filtrate were combined, and the organic phase was 10 separated. The organic phase was dried with anhydrous magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure, leaving a dark oil as a residue. This oil was placed on a silica gel column and eluted with methylene chloride. The 15 product-containing fractions were combined and the solvent evaporated under reduced pressure, leaving 6.8 g of 4-fluorophenylmethyl 4-amino-3-fluorophenyl ether as a solid, m.p. 42-43°C.

Step C: 4-(4-Fluorophenylmethoxy)-2-fluorophenyl
20 isocyanate

To a solution of 6.50 g (0.0276 mole) of 4-fluorophenylmethyl 4-amino-3-fluorophenyl ether in toluene, stirring at room temperature, was slowly added 3.95 g (0.020 mole) of trichloromethyl chloroformate. During 25 the addition a thick precipitate formed. Upon completion of addition, the reaction mixture was stirred for one hour at room temperature and then at reflux for approximately seventeen hours. The toluene was removed by distillation, leaving 7.10 g of 4-(4-fluorophenylmethoxy)-2-fluorophenyl isocyanate.

Step D: 1-[4-(4-Fluorophenylmethoxy)-2-fluorophenyl]-
30 1,4-dihydro-5H-tetrazol-5-one

A mixture of 7.10 g (0.027 mole) of 4-(4-fluorophenylmethoxy)-2-fluorophenyl isocyanate and 7.0 g (0.060 mole) of trimethylsilyl azide was heated at 35 reflux for approximately seventeen hours. The solution

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was then allowed to cool to room temperature before being poured over ice. A solid formed and was recovered by filtration. The solid was dried, leaving 8.08 g of 1-[4-(4-fluorophenylmethoxy)-2-fluorophenyl]-
5 1,4-dihydro-5H-tetrazol-5-one, m.p. 171-172°C.

Step E: 1-[4-(4-Fluorophenylmethoxy)-2-fluorophenyl]-
1,4-dihydro-4-(3-fluoropropyl)-5H-tetrazol-5-
one

A mixture of 7.0 g (0.023 mole) of 1-[4-(4-fluoro-
10 phenylmethoxy)-2-fluorophenyl]-1,4-dihydro-5H-tetrazol-
5-one, 4.23 g (0.030 mole) of 1-bromo-3-fluoropropane,
and 4.14 g (0.030 mole) of anhydrous potassium
carbonate in 60 mL of N,N-dimethylformamide was heated
at 70°C for approximately seventeen hours. The mixture
15 was allowed to cool to room temperature before being
poured over ice. The solid that formed was removed by
filtration and dried. This solid was then placed on a
silica gel column and eluted with methylene
chloride. The product-containing fractions were
20 combined and the solvents evaporated under reduced
pressure, leaving 6.35 g of 1-[4-(4-fluorophenyl-
methoxy)-2-fluorophenyl]-1,4-dihydro-4-(3-fluoro-
propyl)-5H-tetrazol-5-one, m.p. 86-88°C.

Step F: 1-(2-Fluoro-4-hydroxyphenyl)-1,4-dihydro-4-(3-
25 fluoropropyl)-5H-tetrazol-5-one

To a solution of 5.60 g (0.0153 mole) of 1-[4-(4-
fluorophenylmethoxy)-2-fluorophenyl]-1,4-dihydro-4-(3-
fluoropropyl)-5H-tetrazol-5-one in 60 mL of glacial
acetic acid was added 5 mL of 49% hydrobromic acid.
30 This mixture was heated at reflux for 90 minutes, after
which it was cooled to room temperature. The reaction
mixture was then poured over ice, and the resulting
aqueous solution was extracted with diethyl ether. The
combined extract was dried over magnesium sulfate,
35 filtered, and the solvent was evaporated under reduced
pressure, leaving 4.35 g of 1-(2-fluoro-4-hydroxy-

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phenyl)-1,4-dihydro-4-(3-fluoropropyl)-5H-tetrazol-5-one as a residue.

Step G: Methyl 2-[2-[4-[1,4-dihydro-4-(3-fluoropropyl)-5H-tetrazol-5-on-1-yl]-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate

By the method Example 1, Step I, 0.85 g (0.0033 mole) of 1-(2-fluoro-4-hydroxyphenyl)-1,4-dihydro-4-(3-fluoropropyl)-5H-tetrazol-5-one and 1.21 g (0.0050 mole) of methyl 2-(2-chloromethyl-5-methylphenoxy)propionate (Example 1, Step H) were reacted in the presence of 0.70 g (0.0050 mole) of anhydrous potassium carbonate in 60 mL of N,N-dimethylformamide, yielding 0.42 g of methyl 2-[2-[4-[1,4-dihydro-4-(3-fluoropropyl)-5H-tetrazol-5-on-1-yl]-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate as an oil. The NMR spectrum was consistent with the proposed structure. NMR: 1.64 (d, 3H, $J_{HH} = 8$ Hz); 2.2-2.4 (m, 2H); 2.32 (s, 3H); 3.72 (s, 3H); 4.18 (t, 2H, $J_{HH} = 8$ Hz); 4.50-4.64 (dt, 2H, $J_{HH} = 8$ Hz, $J_{HF} = 45$ Hz); 4.84 (q, 1H, $J_{HH} = 8$ Hz), 5.20 (q, 2H, $J_{HH} = 8$ Hz); 6.58-7.40 (m, 6H).

EXAMPLE 5

METHYL 2-[2-[4-(3-CHLORO-4,5,6,7-TETRAHYDROINDAZOL-2-YL)-3-FLUOROPHOXYMETHYL]-5-CHLOROPHOXY]PROPIONATE
(Compound 66)

Step A: 2-Fluoro-4-methoxyphenylhydrazine

With vigorous stirring, 9.15 g (0.065 mole) of 2-fluoro-4-methoxyaniline was added to 60 mL of concentrated hydrochloric acid that had been cooled to -10°C. A solution of 4.83 g (0.070 mole) of sodium nitrite in 30 mL of water was slowly added dropwise, while the temperature was kept at or below -10°C. Upon completion of addition, the reaction mixture was stirred at -10°C for one hour, after which 33.85 (0.150 mole) of tin(II) chloride dihydrate in 50 mL of concentrated hydrochloric acid was added slowly, dropwise, while the temperature was kept below -5°C.

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After the reaction mixture had stirred for one hour as it warmed to ambient temperature, the crude product was filtered from the mixture and dissolved in 250 mL of water. This solution was made basic with 4N sodium hydroxide and extracted with methylene chloride. The combined extracts were dried over anhydrous sodium sulfate and filtered. The filtrate was placed on a silica gel column and eluted with methylene chloride to remove colored impurities and then with ethyl acetate to obtain the desired product. The solvent was evaporated under reduced pressure to yield 6.30 g of 2-fluoro-4-methoxyphenylhydrazine. The NMR spectrum was consistent with the proposed structure.

Step B: 2-(2-Fluoro-4-methoxyphenyl)-4,5,6,7-tetra-
15 hydro-1H-indazol-3-one

To a solution of 6.28 g (0.040 mole) of 2-fluoro-4-methoxyphenylhydrazine in 200 mL of toluene was added with stirring 6.82 g (0.040 mole) of ethyl 2-cyclohexanonecarboxylate. This mixture was heated at reflux under a nitrogen atmosphere while water was removed with a Dean-Stark trap. When all water had been removed, the reaction mixture was cooled, and the solvent was evaporated under reduced pressure, leaving a residue which was then dissolved in acetic acid. This solution was heated at reflux for approximately sixteen hours, after which the solvent was evaporated under reduced pressure, leaving a residue. This residue was dissolved in toluene, which was also evaporated under reduced pressure. The residue was dissolved in ethyl acetate and placed on a silica gel column and eluted with ethyl acetate. An attempt to crystallize the product by dissolving it in diethyl ether after the ethyl acetate had been evaporated was unsuccessful. After the solvent had been evaporated from this product, it was again heated at reflux in acetic acid for 24 hours and allowed to cool to room temperature,

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where the solution stirred for an additional 48 hours. The solvent was evaporated under reduced pressure, leaving a residue weighing 4.32 g. Two additional fractions weighing 0.80 g and 2.75 g had been recovered
5 by extracting the reaction mixture before the solvent was evaporated. The NMR spectrum of the residue showed it to be a mixture of 2-(2-fluoro-4-methoxyphenyl)-
4,5,6,7-tetrahydro-1H-indazol-3-one and the 2-fluoro-4-methoxyphenylhydrazone of 2-cyclohexanonecarboxylic acid.
10

Step C: 3-Chloro-2-(2-fluoro-4-methoxyphenyl)-4,5,6,7-tetrahydro-1H-indazole

The 4.32 g residue from Step B was mixed at ambient temperature with 5.37 g (0.035 mole) of phosphorus oxychloride until complete dissolution occurred. At this point the reaction mixture was heated at reflux under nitrogen for one hour. The phosphorus oxychloride was evaporated from the reaction mixture under reduced pressure, leaving a residue weighing 1.50 g. This residue, together with a similar residue weighing 0.30 g from an earlier experiment, was then placed on a silica gel column and eluted with hexane/ethyl acetate (4:1). After the product-containing fractions were combined and the solvents evaporated under reduced pressure, 0.50 g of 3-chloro-2-(2-fluoro-4-methoxyphenyl)-4,5,6,7-tetrahydroindazole was isolated. The NMR was consistent with the proposed structure.

Step D: 3-Chloro-2-(2-fluoro-4-hydroxyphenyl)-4,5,6,7-tetrahydroindazole

30 A 1N solution of boron tribromide in methylene chloride (18.0 mL, 0.018 mole) was diluted with 17 mL of methylene chloride and was then cooled to below -10°C under a nitrogen atmosphere. A solution of 3-chloro-2-(2-fluoro-4-methoxyphenyl)-4,5,6,7-tetrahydroindazole in 25 mL of methylene chloride was added dropwise at a rate to maintain the temperature below -10°C.

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Upon completion of addition, the reaction mixture was allowed to warm to ambient temperature at which it stirred for sixteen hours. The mixture was then poured into ice-water, and the resulting mixture was stirred 5 for 30 minutes. This mixture was filtered, and the filtrate was passed through a short column of silica gel. The organic phase was separated, dried with anhydrous sodium sulfate, and filtered. The solvent was evaporated from the filtrate under reduced 10 pressure, leaving 0.60 g of 3-chloro-2-(2-fluoro-4-hydroxyphenyl)-4,5,6,7-tetrahydroindazole as a nearly white solid, m.p. 214-216°C. The NMR and IR spectra were consistent with the proposed structure.

Step E: Methyl 2-[2-[4-(3-chloro-4,5,6,7-tetrahydro-indazol-2-yl)-3-fluorophenoxy]methyl]-5-chlorophenoxy]propionate

By the method of Example 1; Step I, 0.49 g (0.0016 mole) of 3-chloro-2-(2-fluoro-4-hydroxyphenyl)-4,5,6,7-tetrahydroindazole and 0.52 g (0.002 mole) of methyl 2-(2-chloromethyl-5-chlorophenoxy)propionate (Example 2, Step E) were reacted in the presence of 0.41 g (0.003 mole) of anhydrous potassium carbonate in 30 mL of N,N-dimethylformamide, yielding 0.64 g of methyl 2-[2-[4-(3-chloro-4,5,6,7-tetrahydroindazol-2-yl)-3-fluorophenoxy]methyl]-5-chlorophenoxy]propionate as a syrup. 20 The NMR and IR spectra were consistent with the proposed structure. NMR: 1.64 (d, 3H, $J_{HH} = 8.0$ Hz); 1.82 (m, 4H); 2.50 (t, 2H, $J_{HH} = 4.0$ Hz); 2.68 (t, 2H, $J_{HH} = 4.0$ Hz); 3.76 (s, 3H); 4.82 (q, 1H, $J_{HH} = 8$ Hz); 5.18 (s, 2H,); 6.78-7.40 (m, 6H). 25 30

EXAMPLE 6

METHYL 2-[2-[4-(4-METHYL-1,2,4-TRIAZINE-3,5-DION-2-YL)-3-FLUOROPHOXYMETHYL]-5-METHYLPHENOXY]PROPIONATE
(Compound 70)

35 Step A: 4-Isopropoxy-2-fluoroaniline

A stirred flask containing 350 mL of acetic acid

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was heated to 80-85°C under a nitrogen atmosphere. To this flask was added 39.10 g (0.700 mole) of powdered iron, and this mixture was stirred for one hour. A solution of 4-isopropoxy-2-fluoronitrobenzene in 250 mL
5 was added to the mixture dropwise. Upon completion of addition, the reaction mixture was heated at 80-85°C for one hour. After being cooled below 40°C, the mixture was filtered, and the solvent was evaporated under reduced pressure, leaving a residue. This residue
10 due was dissolved in a mixture of water and diethyl ether. The organic layer was separated and was washed in succession with saturated aqueous solutions of sodium bicarbonate and sodium chloride. It was then dried over anhydrous magnesium sulfate, filtered
15 through a short column of silica gel, and the solvent was evaporated under reduced pressure, leaving an impure residue which contained significant amounts of acetamide in addition to the desired product. This residue was suspended in 500 mL of 2N hydrochloric acid
20 for one hour. The hydrochloric acid mixture was then extracted with diethyl ether, and the two phases were separated. Aqueous sodium hydroxide solution was added to the aqueous hydrochloride solution until it was basic. This basic solution was extracted with diethyl
25 ether, and the extract was dried over anhydrous magnesium sulfate and filtered. After evaporation of the solvent under reduced pressure, the residue was recrystallized from diethyl ether/petroleum ether to yield 16.90 g of 4-isopropoxy-2-fluoroaniline as an oil
30 which darkened on standing. The NMR spectrum was consistent with the proposed structure.

Step B: Malonyldiurethane

With a mortar and pestle 10.40 g (0.100 mole) of malonic acid and 18.00 g (0.210 mole) of ethyl carbamate were ground to a fine powder. This powder
35 was placed in a flask, and 16.0 mL (0.167 mole) of

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phosphorus oxychloride was added. This mixture was heated at 80°C until the evolution of gas ceased. After this reaction mixture had cooled to ambient temperature, 210 mL of water was added. When the stiff glassy mixture became fluid, it was extracted with ethyl acetate. The combined extracts were washed in succession with saturated aqueous solutions of sodium bicarbonate and sodium chloride and were then dried over anhydrous magnesium sulfate and filtered. The solution was filtered through a short column of silica gel, which was eluted with ethyl acetate. The solvent was then evaporated under reduced pressure, leaving a crystalline mass of malonyldiurethane weighing 10.62 g. The NMR spectrum was consistent with the proposed structure.

Step C: 2-(4-Isopropoxy-2-fluorophenyl)hydrazone-malonyldiurethane

A mixture of 5.92 g (0.035 mole) of 4-isopropoxy-2-fluoroaniline, 10.60 g (0.043 mole) of malonyldiurethane, and 41.02 g (0.500 mole) of sodium acetate was suspended in 1000 mL of water with vigorous stirring. To this suspension was added 25 mL of 12 N hydrochloric acid. The reaction mixture was cooled to 10°C, and, while this temperature was maintained, a solution of 2.42 g (0.035 mole) of sodium nitrite in 25 mL of water was slowly added. The reaction mixture was allowed to warm slowly to room temperature where it was stirred under a nitrogen atmosphere for approximately 16 hours. During this period a yellow solid formed and precipitated out. The mixture was filtered, and the yellow solid was washed in succession with water and diethyl ether. After being dried, 9.20 g of 2-(4-isopropoxy-2-fluorophenyl)hydrazone malonyldiurethane was isolated as a yellow solid. The NMR and IR spectra were consistent with the proposed structure.

Step D: 2-(4-Isopropoxy-2-fluorophenyl)-1,2,4-

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triazine-3,5-dion-6-carboxylic acid

To a stirred solution of 8.94 g (0.021 mole) of 2-(4-isopropoxy-2-fluorophenyl)hydrazonomalonyldiurethane in 125 mL of ethanol and 125 mL of tetrahydrofuran was
5 added 75 mL (0.134 mole) of 10% aqueous potassium hydroxide, initially forming a precipitate, which subsequently dissolved. After this mixture was stirred for 30 minutes at ambient temperature, 30 mL of 11.7 N hydrochloric acid was added carefully with stirring.
10 The tetrahydrofuran was evaporated under reduced pressure, and the residue was then extracted with ethyl acetate. The combined extracts were treated with decolorizing charcoal, dried over anhydrous magnesium sulfate, and filtered through a short column of silica
15 gel, which was eluted with ethyl acetate. The solvent was evaporated from the filtrate, yielding 4.70 g of 2-(4-isopropoxy-2-fluorophenyl)-1,2,4-triazine-3,5-dion-6-carboxylic acid as an amorphous foam. The NMR spectrum was consistent with the proposed structure.
20 Step E: 2-(4-Isopropoxy-2-fluorophenyl)-1,2,4-triazine-3,5-dione
A solution of 4.70 g (0.0152 mole) of 2-(4-isopropoxy-2-fluorophenyl)-1,2,4-triazine-3,5-dion-6-carboxylic acid in 5 mL of mercaptoacetic acid was heated at
25 140-145°C for two hours under a nitrogen atmosphere. After this mixture had cooled, it was poured into 250 mL of a saturated aqueous solution of sodium bicarbonate with vigorous stirring. An equal volume of ethyl acetate was added to this mixture, and the
30 resulting layers were separated. The organic layer was washed twice with 150 mL of a saturated aqueous solution of sodium bicarbonate and once with 150 mL of a saturated aqueous solution of sodium chloride. The organic solution was then dried over anhydrous magnesium sulfate and filtered. The solvent was
35 evaporated under reduced pressure, leaving a syrup

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which slowly crystallized to a yellow-orange solid upon standing. This solid was recrystallized from ethyl acetate/petroleum ether (1:1), yielding 0.60 g of 2-(4-isopropoxy-2-fluorophenyl)-1,2,4-triazine-3,5-dione as a yellow solid. The NMR was consistent with the proposed structure. This reaction was repeated to obtain additional material for subsequent reactions.

Step F: 2-(4-Isopropoxy-2-fluorophenyl)-4-methyl-1,2,4-triazine-3,5-dione

10 A solution of 3.25 g (0.0123 mole) of 2-(4-isopropoxy-2-fluorophenyl)-1,2,4-triazine-3,5-dione in 30 mL of N,N-dimethylformamide was added to a suspension of 0.50 g (0.0125 mole) of sodium hydride in 30 mL of N,N-dimethylformamide at ambient temperature. When gas evolution had ceased, 3.55 g (0.025 mole) of iodo-methane was added in one portion. This mixture was stirred for one hour without heating, and was then poured into 300 mL of dilute hydrochloric acid. The resulting mixture was extracted several times with diethyl ether, and the extracts were combined. The ether extract was washed in succession with water and a saturated aqueous solution of sodium chloride. It was then dried over anhydrous magnesium sulfate and filtered through a short column of silica gel. The solvent was evaporated under reduced pressure, leaving 2.80 g of 2-(4-isopropoxy-2-fluorophenyl)-4-methyl-1,2,4-triazine-3,5-dione as a syrup. The NMR was consistent with the proposed structure.

Step G: 2-(4-Hydroxy-2-fluorophenyl)-4-methyl-1,2,4-triazine-3,5,-dione

Concentrated sulfuric acid (5 mL) that had been cooled to 0-5°C was mixed with 2.80 g (0.010 mole) of 2-(4-isopropoxy-2-fluorophenyl)-4-methyl-1,2,4-triazine-3,5-dione that had been cooled to 0°C. The mixture was maintained at 0°C for ten minutes, during which time it became homogeneous. The mixture was then

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poured into ice-water, and the resulting mixture was extracted with ethyl acetate. The extract was washed in succession with a saturated aqueous solution of sodium bicarbonate and a saturated aqueous solution of 5 sodium chloride. The extract was dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated from the filtrate under reduced pressure, leaving a residue. This residue was placed on a column of silica gel and eluted with ethyl acetate/hexane 10 (1:1). After the product-containing fractions were combined and the solvents evaporated under reduced pressure, 1.38 g of 2-(4-hydroxy-2-fluorophenyl)-4-methyl-1,2,4-triazine-3,5-dione was recovered as a stiff syrup. The NMR was consistent with the proposed 15 structure.

Step H: Methyl 2-[2-[4-(4-methyl-1,2,4-triazine-3,5-dion-2-yl)-3-fluorophenoxy]methyl]-5-methyl-phenoxy]propionate

By the method of Example 1, Step I, 0.47 g (0.002 mole) of 2-(4-hydroxy-2-fluorophenyl)-4-methyl-1,2,4-triazine-3,5-dione and 0.73 g (0.003 mole) of methyl 2-(2-chloromethyl-5-methylphenoxy)propionate were reacted in the presence of 0.41 g (0.003 mole) of anhydrous potassium carbonate in 30 mL of N,N-dimethylformamide, 25 yielding 0.70 g of methyl 2-[2-[4-(4-methyl-1,2,4-triazine-3,5-dion-2-yl)-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate as a syrup. The IR and NMR spectra were consistent with the proposed structure. NMR: 1.60 (d, 3H, $J_{HH} = 8.0$ Hz); 2.30 (s, 3H); 3.40 (s, 3H); 3.78 (s, 3H); 4.84 (q, 1H, $J_{HH} = 8.0$ Hz); 5.18 (dd, 2H, $J_{HH} = 10$ Hz); 6.58 (s, 1H); 6.8-7.3 (m, 5H); 30 7.54 (s, 1H).

EXAMPLE 7

METHYL 2-[2-[4-(4-DIFLUOROMETHYL-4,5-DIHYDRO-3-METHYL-
35 1,2,4-TRIAZOL-5(1H)-ON-1-YL)-3-FLUOROPHENYLTHIO-METHYL]-5-CHLOROPHOXY]PROPIONATE

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(Compound 72)

Step A 4-(4-Difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenyl-sulfonyl chloride

5 A mixture of 2.02 g (0.0078 mole) of 1-(2-fluoro-4-aminophenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4,-triazol-5(1H)-one (Example 1, Step D) in 20 mL of hydrochloric acid was cooled to 0°C, and 0.55 g (0.0084 mole) of sodium nitrite in 5 mL of water was
10 added slowly while the temperature was held at 0-5°C. The yellow solution was then stirred at room temperature for two hours. Meanwhile a solution of 1.08 g (0.0080 mole) of copper(II) chloride in 5 mL of water and 20 mL of acetic was prepared, and sulfur
15 dioxide was bubbled through this solution until it was saturated, a period of ten minutes. After having been stirred for two hours, the yellow solution was added slowly to the solution saturated with sulfur dioxide. The mixture turned green, and a yellow precipitate
20 formed. During the addition, the temperature rose to 32°C. The reaction mixture was stirred for an hour at room temperature and then poured over ice. The pale yellow solid that formed was isolated by filtration, yielding 1.86 g of 4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenyl-sulfonyl chloride. The NMR spectrum was consistent with the proposed structure. This reaction was repeated to obtain additional product for subsequent reactions.

25 Step B 4-(4-Difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorothio-phenol
30 Gaseous hydrogen chloride was bubbled into a mixture of 3.29 g (0.0146 mole) of tin(II) chloride in 40 mL of acetic acid for about five minutes, causing it to become a clear solution. This solution was then

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heated to 85°C, and a hot solution of 1.66 g (0.00485 mole) of 4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenylsulfonyl chloride was added to the first solution. This
5 reaction mixture was heated at 85°C for 45 minutes. After cooling to room temperature, the resulting yellow solution was poured into 120 mL of hydrochloric acid. To this mixture was added 100 mL of a saturated aqueous solution of sodium chloride, and the resulting mixture
10 was extracted with ethyl acetate, but the layers did not separate. The addition of a saturated aqueous solution of sodium chloride did effect a partial separation. The aqueous layer was extracted two more times with ethyl acetate, and all extracts were com-
15 bined. After evaporation of the solvent under reduced pressure, the residue retained an odor of hydrochloric acid. Water was added to the residue, and this mixture was extracted three times with ethyl acetate. The combined extracts were washed with water, dried over
20 anhydrous magnesium sulfate, and filtered. Following evaporation of the solvent under reduced pressure, the yellow residue that remained was dried under vacuum. This dried residue was placed on a column of silica gel and eluted with methylene chloride/ethyl acetate (2:1).
25 After being dried under vacuum for several hours, 0.81 g of 4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorothiophenol was isolated as a yellow syrup. The NMR spectrum was consistent with the proposed structure. This reaction was
30 repeated to obtain additional product for subsequent reactions.

Step C Methyl 2-[2-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenylthiomethyl]-5-chlorophenoxy]-propionate
35

By the method of Example 1, Step I, 1.35 g (0.0049

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mole) of 4-(4-difluoromethyl-4,5-dihydro-3-methyl-
1,2,4-triazol-5(1H)-on-1-yl)-3-fluorothiophenol and 3.0
g (0.011 mole) of methyl 2-(2-chloromethyl-5-chloro-
phenoxy)propionate (Example 2, Step E) were reacted in
5 the presence of 1.02 g (0.0074 mole) of anhydrous
potassium carbonate in 75 mL of N,N-dimethylformamide,
yielding 0.54 g of methyl 2-[2-[4-(4-difluoromethyl-
4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-
fluorophenylthiomethyl]-5-chlorophenoxy]propionate as a
10 yellow syrup. The NMR spectrum was consistent with the
proposed structure. NMR: 1.65 (d, 3H, $J_{HH} = 8.0$ Hz);
2.44 (s, 3H); 3.78 (s, 3H); 4.20 (dd, 2H, $J_{HH} = 13.0$
Hz); 4.78 (q, 1H, $J_{HH} = 8.0$ Hz); 6.70-7.38 (m, 7H).

EXAMPLE 8

15 METHYL [2-[4-(4-DIFLUOROMETHYL-4,5-DIHYDRO-3-METHYL-
1,2,4-TRIAZOL-5(1H)-ON-1-YL)-3-FLUOROPHOXYMETHYL]-5-
METHYLPHENOXY]ACETATE

(Compound 75)

Step A Methyl (2-formyl-5-methylphenoxy)acetate

20 By the method of Example 1, Step F, 8.27 g (0.060
mole) of 4-methylsalicylaldehyde and 11.15 g (0.073
mole) of methyl bromoacetate were reacted in the
presence of 10.1 g (0.073 mole) of anhydrous potassium
carbonate in 150 mL of acetone, yielding 11.47 g of
25 methyl (2-formyl-5-methylphenoxy)acetate as a white
solid, m. p. 63-64°C. The NMR was consistent with the
proposed structure.

Step B Methyl (2-hydroxymethyl-5-methylphenoxy)-
acetate

30 By the method of Example 1, Step G, 11.27 g (0.054
mole) of methyl (2-formyl-5-methylphenoxy)acetate was
reacted with 0.54 g (0.014 mole) of sodium borohydride
and 0.10 g (0.0018 mole) of sodium methoxide in 30 mL
of methanol, yielding 9.41 g of methyl (2-hydroxymeth-
35 yl-5-methylphenoxy)acetate as a yellow oil. The NMR
spectrum was consistent with the proposed structure.

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Step C Methyl (2-chloromethyl-5-methylphenoxy)acetate

By the method of Example 1, Step H, 9.21 g (0.044 mole) of methyl (2-hydroxymethyl-5-methylphenoxy)acetate was reacted with 7.40 g (0.062 mole) of thionyl chloride and 5 drops of pyridine in 50 mL of methylene chloride, yielding 5.57 g of methyl (2-chloromethyl-5-methylphenoxy)acetate as an orange liquid.

Step D Methyl [2-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenoxy]methyl]-5-methylphenoxy]acetate

By the method of Example 1, Step I, 2.0 g (0.0077 mole) of 1-(2-fluoro-4-hydroxyphenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one (Example 1, Step E) and 3.53 g (0.0151 mole) of methyl (2-chloromethyl-5-methylphenoxy)acetate were reacted in the presence of 1.60 g (0.0116 mole) of anhydrous potassium carbonate in 40 mL of N,N-dimethylformamide, yielding 2.75 g of methyl [2-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenoxy]methyl]-5-methylphenoxy]acetate. The NMR spectrum was consistent with the proposed structure.
NMR: 2.30 (s, 3H); 2.44 (s, 3H); 3.78 (s, 3H); 4.70 (s, 2H); 5.18 (s, 2H); 6.60-7.36 (m, 7H).

EXAMPLE 9

**2-[3-[4-(4-DIFLUOROMETHYL-4,5-DIHYDRO-3-METHYL-1,2,4-TRIAZOL-5(1H)-ON-1-YL)-3-FLUOROPHOXYMETHYL]-PHENOXY]PROPIONATE
(Compound 80)**

Step A Methyl 2-(3-formylphenoxy)propionate

By the method of Example 1, Step F, 10.0 g (0.0819 mole) of 3-hydroxybenzaldehyde and 16.0 g (0.0982 mole) of methyl 2-bromopropionate were reacted in the presence of 13.6 g (0.0983 mole) of anhydrous potassium carbonate in 50 mL of N,N-dimethylformamide, yielding 16.1 g of methyl 2-(3-formylphenoxy)propionate as an orange liquid. The NMR and IR spectra were consistent

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with the proposed structure.

Step B Methyl 2-(3-hydroxymethylphenoxy)propionate

By the method of Example 1, Step G, 15.7 g (0.0761 mole) of methyl 2-(3-formylphenoxy)propionate, 0.76 g (0.020 mole) of sodium borohydride, and 0.10 g (0.0018 mole) of sodium methoxide were reacted in 40 mL of methanol, yielding 15.6 g of methyl 2-(3-hydroxymethylphenoxy)propionate as a yellow liquid. The NMR and IR spectra were consistent with the proposed structure.

10 Step C Methyl 2-(3-chloromethylphenoxy)propionate

By the method of Example 1, Step H, 1.98 g (0.0095 mole) of methyl 2-(3-hydroxymethylphenoxy)propionate and 1.24 g (0.0105 mole) of thionyl chloride were reacted in the presence of five drops of pyridine in 40 mL of methylene chloride, yielding 1.93 g of methyl 2-(3-chloromethylphenoxy)propionate as a yellow liquid. The NMR and IR spectra were consistent with the proposed structure.

20 Step D Methyl 2-[3-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenoxy]phenoxy]propionate

By the method of Example 1, Step I, 1.0 g (0.0038 mole) of 1-(2-fluoro-4-hydroxyphenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one (Example 1, Step F) and 1.72 g (0.0076 mole) of methyl 2-(3-chloromethylphenoxy)propionate were reacted in the presence of 0.79 g (0.0057 mole) of anhydrous potassium carbonate in 25 mL of N,N-dimethylformamide, yielding 1.54 g of methyl 2-[3-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenoxy]phenoxy]propionate. The NMR and IR spectra were consistent with the proposed structure. NMR: 1.60 (d, 3H, J_{HH} = 8.0 Hz); 2.44 (s, 3H); 3.76 (s, 3H); 4.78 (q, 1H, J_{HH} = 8.0 Hz); 5.04 (s, 2H); 6.76-7.38 (m, 8H).

35 EXAMPLE 10

METHYL 2-[4-[4-(4-DIFLUOROMETHYL-4,5-DIHYDRO-3-METHYL-

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1,2,4-TRIAZOL-5(1H)-ON-1-YL)-3-FLUOROPHOXYMETHYL]-
PHENOXY]PROPIONATE
(Compound 81)

Step A Methyl 2-(4-formylphenoxy)propionate
5 By the method of Example 1, Step F, 10.0 g (0.0819 mole) of 4-hydroxybenzaldehyde and 16.4 g (0.0983 mole) of methyl 2-bromopropionate were reacted in the presence of 13.6 g (0.0983 mole) of anhydrous potassium carbonate in N,N-dimethylformamide, yielding 12.2 g of
10 methyl 2-(4-formylphenoxy)propionate as a yellow liquid. The NMR and IR spectra were consistent with the proposed structure.

Step B Methyl 2-(4-hydroxymethylphenoxy)propionate
15 By the method of Example 1, Step G, 11.1 g (0.0533 mole) of methyl 2-(4-formylphenoxy)propionate and 2.02 g (0.0533 mole) of sodium borohydride were reacted in methanol, yielding 9.31 g of methyl 2-(4-hydroxymethylphenoxy)propionate as a yellow oil. The NMR spectrum was consistent with the proposed structure.

20 Step C Methyl 2-(4-chloromethylphenoxy)propionate
A mixture of 2.19 g (0.0104 mole) of methyl 2-(4-hydroxymethylphenoxy)propionate and 3.00 g (0.0823 mole) of 36% hydrochloric acid was stirred for fifteen minutes at room temperature. The reaction mixture was
25 then poured into ice-water, and the resulting mixture was extracted with diethyl ether. The extracts were combined and washed in succession with water and a saturated aqueous solution of sodium bicarbonate. The extract was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated from the filtrate under reduced pressure, leaving a colorless liquid. This liquid was placed on a column of silica gel and eluted with methylene chloride. After the product-containing fractions were combined and the
30 solvent evaporated under reduced pressure, 1.6 g of methyl 2-(4-chloromethylphenoxy)propionate was isolated
35

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as a colorless liquid. The NMR and IR spectra were consistent with the proposed structure.

Step D Methyl 2-[4-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenoxy]phenoxy]propionate

By the method of Example 1, Step I, 0.50 g (0.0019 mole) of 1-(2-fluoro-4-hydroxyphenyl)-4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-one (Example 1, Step E) and 0.87 g (0.0038 mole) of methyl 2-(4-chloromethylphenoxy)propionate were reacted in the presence of 0.2 g of 1,4,7,10,13,16-hexaoxacyclooctadecane in 25 mL of N,N-dimethylformamide, yielding 0.80 g of methyl 2-[4-[4-(4-difluoromethyl-4,5-dihydro-3-methyl-1,2,4-triazol-5(1H)-on-1-yl)-3-fluorophenoxy]methyl]phenoxy]propionate as a colorless oil that solidified upon standing, m.p. 83-85°C. The NMR and IR spectra were consistent with the proposed structure.
NMR: 1.60 (d, 3H, J_{HH} = 8.0 Hz); 2.44 (s, 3H); 3.76 (s, 3H); 4.78 (q, 1H, J_{HH} = 8.0 Hz); 4.90 (s, 2H); 6.78-7.38 (m, 8H).

EXAMPLE 11

METHYL 2-[2-[4-(8-THIA-1,6-DIAZABICYCLO[4.3.0]NONANE-7-ON-9-YLIMINO)-3-FLUOROPHOXYMETHYL]-5-METHYLPHENOXY]-PROPIONATE
(Compound 68)

Step A Methyl 2-[2-(3-fluoro-4-nitrophenoxy)methyl]-5-methylphenoxy]propionate

By the method of Example 1, Step I, 1.71 g (0.010 mole) of 3-fluoro-4-nitrophenol and 2.85 g (0.011 mole) of methyl 2-(2-chloromethyl-5-methylphenoxy)propionate were reacted in the presence of 1.66 g (0.012 mole) of anhydrous potassium carbonate in 100 mL of N,N-dimethylformamide, yielding 3.55 g of methyl 2-[2-(3-fluoro-4-nitrophenoxy)methyl]-5-methylphenoxy]propionate as a yellowish solid, m.p. 92-94°C. The NMR and IR spectra were consistent with the proposed structure.

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Step B Methyl 2-[2-(4-amino-3-fluorophenoxyethyl)-5-methylphenoxy]propionate

By the method of Example 2, Step A, 3.35 g (0.0091 mole) of methyl 2-[2-(3-fluoro-4-nitrophenoxyethyl)-5-methylphenoxy]propionate was reacted with 2.80 g (0.050 mole) of powdered iron in 100 mL of acetic acid, yielding 1.86 g of methyl 2-[2-(4-amino-3-fluorophenoxyethyl)-5-methylphenoxy]propionate as an amber syrup. The NMR and IR spectra were consistent with the proposed structure.

Step C Methyl 2-[2-(3-fluoro-4-isothiocyanatophenoxy-methyl)-5-methylphenoxy]propionate

A solution of 1.66 g (0.005 mole) of methyl 2-[2-(4-amino-3-fluorophenoxyethyl)-5-methylphenoxy]propionate and 1.26 g (0.0125 mole) of triethylamine in 40 mL of methylene chloride was prepared at ambient temperature. To this solution was added dropwise a solution of 0.58 g (0.0050 mole) of thiophosgene in 10 mL of methylene chloride. The reaction mixture was stirred for 16 hours after which it was filtered through a short column of silica gel. The solvent was evaporated from the filtrate under reduced pressure, leaving 1.50 g of methyl 2-[2-(3-fluoro-4-isothiocyanatophenoxyethyl)-5-methylphenoxy]propionate as a syrup. The NMR and IR spectra were consistent with the proposed structure.

Step D Methyl 2-[2-[4-(perhydropyridazin-1-ylthio-carbonylamino)-3-fluorophenoxyethyl]-5-methylphenoxy]propionate

By the method of Example 1, Step C, of U. S. 4,906,281, 1.50 g (0.004 mole) of methyl 2-[2-(3-fluoro-4-isothiocyanatophenoxyethyl)-5-methylphenoxy]propionate and 1.07 g (0.005 mole) of perhydropyridazine monohydroiodide (prepared by the method of Example 1, Step B, of U. S. 4,906,281) were reacted in the presence of 0.20 g (0.0050 mole of sodium hydroxide

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in 40 mL of water and 10 mL of tetrahydrofuran, yielding 1.50 g of methyl 2-[2-[4-(perhydropyridazin-1-ylthiocarbonylamino)-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate as a syrup. The NMR spectrum was
5 consistent with proposed structure.

Step E Methyl 2-[2-[4-(8-thia-1,6-diazabicyclo[4.3.0]nonane-7-on-9-ylimino)-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate
By the method of Example 1, Step D, of U. S.
10 4,906,281, 1.50 g (0.00325 mole) of methyl 2-[2-[4-(perhydropyridazin-1-ylthiocarbonylamino)-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate and 0.36 g (0.09017 mole) of trichloromethyl chloroformate were reacted in the presence of 0.36 g (0.0035 mole) of
15 triethylamine in 35 mL of dioxane, yielding 0.50 g of methyl 2-[2-[4-(8-thia-1,6-diazabicyclo[4.3.0]nonane-7-on-9-ylimino)-3-fluorophenoxy]methyl]-5-methylphenoxy]propionate as a syrup. The NMR and IR spectra were consistent with the proposed structure. NMR: 1.60 (d,
20 3H, $J_{HH} = 8.0$ Hz); 1.78-1.96 (m, 4H); 2.30 (s, 3H); 3.64-3.80 (m, 4H); 3.70 (s, 3H); 4.80 (q, 1H, $J_{HH} = 8.0$ Hz); 5.10 (dd, 2H); 6.58-7.30 (m, 6H).

EXAMPLE 12

METHYL 2-[2-[4-1-METHYL-7-TRIFLUOROMETHYL-2,4-(1H,3H)-
25 PYRIMIDINEDION-3-YL)PHENOXYMETHYL]-5-METHYLPHENOXY]-
PROPIONATE
(Compound 87)

Step A 1-Methyl-3-(4-methoxyphenyl)-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedione
30 In a flask was placed 8.27 g (0.207 mole) of a 60% suspension of sodium hydride in mineral oil. The mineral oil was removed by washing the sodium hydride twice with heptane. To the flask was then added 300 mL of tetrahydrofuran. This suspension was cooled to
35 -20°C at which it was maintained during the dropwise addition of 37.9 g (0.207 mole) of 3-amino-4,4,4-

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trifluorocrotonate. This mixture was allowed to stir for 10 minutes before the dropwise addition of 30.83 g (0.207 mole) of 4-methoxyphenyl isocyanate was commenced. Upon completion of addition, the reaction 5 mixture was heated at reflux for approximately 16 hours. At the conclusion of this period the reaction mixture was cooled to ambient temperature, and 28.56 g (0.207 mole) of potassium carbonate and 58.75 g (0.228 mole) of methyl iodide were added to it. The reaction 10 mixture was then heated at reflux for seven hours. At the conclusion of this period the reaction mixture was cooled, and diethyl ether and water were added to it. The aqueous phase was separated from the organic phase. The latter was washed with water, dried over anhydrous 15 magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure, leaving a residue. This residue was passed through a column of silica gel, eluting with ethyl acetate/heptane mixtures starting with 1:8 and concluding with 1:1. The product- 20 containing fractions were combined, and the solvent was evaporated under reduced pressure, yielding 27.1 g of 1-methyl-3-(4-methoxyphenyl)-6-trifluoromethyl- 2,4(1H,3H)-pyrimidinedione. The NMR spectrum was consistent with the proposed structure.

25 Step B 1-Methyl-3-(4-hydroxyphenyl)-6- trifluoromethyl-2,4(1H,3H)-pyrimidinedione
In a flask were placed 25.88 g (0.086 mole) of 1- 30 methyl-3-(4-methoxyphenyl)-6-trifluoromethyl- 2,4(1H,3H)-pyrimidinedione and 200 mL of methylene chloride. To this flask was added dropwise 258 mL (0.258 mole) of a 1 molar solution of boron tribromide in methylene chloride. Upon completion of addition, 35 this reaction mixture was allowed to stir at ambient temperature for approximately 64 hours after which it was poured over ice. This mixture was filtered to remove insoluble material, and the aqueous and organic

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layers of the filtrate were separated. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated under reduced pressure, leaving 1-methyl-3-(4-hydroxyphenyl)-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedione as a residue. The NMR spectrum was consistent with proposed structure.

Step C Methyl 2-[2-[4-(1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedion-3-yl)phenoxy]methyl]-5-methylphenoxy]propionate

By the method of Example 1, Step I, 0.7 g (0.0029 mole) of methyl 2-(2-chloromethyl-5-methylphenoxy)-propionate (Example 1, Step H), 0.30 g (0.0011 mole) of 1-methyl-3-(4-hydroxyphenyl)-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedione, and 0.22 g (0.0016 mole) of potassium carbonate were reacted in 80 mL of N,N-dimethylformamide, yielding 0.33 g of methyl 2-[2-[4-(1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedion-3-yl)phenoxy]methyl]-5-methylphenoxy]propionate (Compound 87) as a yellow solid, m.p. 52-54°C. The NMR spectrum was consistent with the proposed structure.

Representative compounds of the invention prepared by the methods exemplified above are shown in Table 1. Characterizing data are given in Table 2.

25 HERBICIDAL ACTIVITY

The 2-[(4-heterocyclic-substituted-3-halophenoxy-methyl)phenoxy]alkanoates of this invention were tested in pre- and postemergence evaluations using a variety of broadleaf and grasseous crops and weeds. The test species used to demonstrate the herbicidal activity of these compounds include soybean (Glycine max var. Williams), field corn (Zea mays var. Agway 425X), wheat (Triticum aestivum var. Wheaton), morningglory (Ipomea lacunosa or Ipomea hederacea), velvetleaf (Abutilon theophrasti), green foxtail (Setaria viridis), Johnsongrass (Sorghum halepense), blackgrass

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(Alopecurus myosuroides), common chickweed (Stellaria media), and common cocklebur (Xanthium pensylvanicum). Preparation of Flats

For preemergence testing two disposable fiber flats
5 (8 cm x 15 cm x 25 cm) for each rate of application of
each candidate herbicide were filled to an approximate
depth of 6.5 cm with steam-sterilized sandy loam soil.
The soil was leveled and impressed with a template to
provide five evenly spaced furrows 13 cm long and 0.5
10 cm deep in each flat. Seeds of soybean, wheat, corn,
green foxtail, and Johnsongrass were planted in the
furrows of the first flat, and seeds of velvetleaf,
morningglory, common chickweed, cocklebur, and black-
grass were planted in the furrows of the second flat.
15 The five-row template was employed to firmly press the
seeds into place. A topping soil of equal portions of
sand and sandy loam soil was placed uniformly on top of
each flat to a depth of approximately 0.5 cm. Flats
for postemergence testing were prepared in the same
20 manner, except that they were planted 8-12 days prior
to the preemergence flats and were placed in a green-
house and watered, thus allowing the seeds to germinate
and the foliage to develop.

A stock solution of the candidate herbicide was
25 prepared by dissolving a predetermined weight of the
compound in 20 ml of water/acetone (50/50) containing
0.5% v/v sorbitan monolaurate. Thus for an application
rate of 3000 g/ha of herbicide, 0.21 g of candidate
herbicide was dissolved in 20 ml of the aqueous acetone
30 to prepare the stock solution. For the 300 g/ha rate
of application used in most of the tests reported
below, a 1.0 mL portion of stock solution was diluted
with water/acetone (50/50) to 35 ml, the volume
required for a spray volume of 1000 L/ha. The remain-
35 ing stock solution was then used to prepare spray
solutions for other application rates.

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The spray solution (35 ml) was then sprayed on the four flats simultaneously, i.e., to the surface of the soil of the preemergence flats and to the emerged foliage of the postemergence flats. All flats were
5 placed in the greenhouse, but only the preemergence flats were watered immediately. The foliage of the postemergence flats was kept dry for 24 hours, after which regular watering commenced. Phytotoxicity data, taken as percent control, were recorded 17-21 days
10 after the chemical was applied.

Percent control was determined by a method similar to the 0 to 100 rating system disclosed in "Research Methods in Weed Science," 2nd ed., B. Truelove, Ed.; Southern Weed Science Society; Auburn University,
15 Auburn, Alabama, 1977. The rating system is as follows:

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Herbicide Rating System

<u>Rating Percent Control</u>	<u>Description of Main Categories</u>	<u>Crop Description</u>	<u>Weed Description</u>
0	No effect	No crop reduction or injury	No weed control
10		Slight discoloration or stunting	Very poor weed control
20	Slight effect	Some discoloration, stunting or stand loss	Poor weed control
30		Crop injury more pronounced but not lasting	Poor to deficient weed control
40		Moderate injury, crop usually recovers	Deficient weed control
50	Moderate effect	Crop injury more lasting, recovery doubtful	Deficient to moderate weed control
60		Lasting crop injury, no recovery	Moderate weed control
70		Heavy injury and stand loss	Control somewhat less than satisfactory
80	Severe	Crop nearly destroyed, a few survivors	Satisfactory to good weed control
90		Only occasional live plants left	Very good to excellent
100	Complete effect	Complete crop destruction	Complete weed destruction

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Herbicidal data at 300 or 250 g/ha are presented in Table 2 (preemergence activity) and Table 4 (post-emergence activity). The test compounds are identified in Tables 2 and 3 by numbers which correspond to those in Table 1.

For herbicidal application the active compounds are formulated into herbicidal compositions by admixture in herbicidally effective amounts with adjuvants and carriers normally employed in the art for facilitating the dispersion of active ingredients for the particular utility desired, recognizing the fact that the formulation and mode of application of a toxicant may affect the activity of the material in a given application. Thus, for agricultural use the present herbicidal compounds may be formulated as granules of relatively large particle size, as water-soluble or water-dispersible granules, as powdery dusts, as wettable powders, as emulsifiable concentrates, as solutions, or as any of several other known types of formulations, depending on the desired mode of application.

These herbicidal compositions may be applied either as water-diluted sprays, or dusts, or granules to the areas in which suppression of vegetation is desired. These formulations may contain as little as 0.1%, 0.2% or 0.5% to as much as 95% or more by weight of active ingredient.

Dusts are free flowing admixtures of the active ingredient with finely divided solids such as talc, natural clays, kieselguhr, flours such as walnut shell and cottonseed flours, and other organic and inorganic solids which act as dispersants and carriers for the toxicant; these finely divided solids have an average particle size of less than about 50 microns. A typical dust formulation useful herein is one containing 1.0 part or less of the herbicidal compound and 99.0 parts

of talc.

Wettable powders, also useful formulations for both pre- and postemergence herbicides, are in the form of finely divided particles which disperse readily in water or other dispersant. The wettable powder is ultimately applied to the soil either as a dry dust or as an emulsion in water or other liquid. Typical carriers for wettable powders include Fuller's earth, kaolin clays, silicas, and other highly absorbent, readily wet inorganic diluents. Wettable powders normally are prepared to contain about 5-80% of active ingredient, depending on the absorbency of the carrier, and usually also contain a small amount of a wetting, dispersing or emulsifying agent to facilitate dispersion. For example, a useful wettable powder formulation contains 80.8 parts of the herbicidal compound, 17.9 parts of Palmetto clay, and 1.0 part of sodium lignosulfonate and 0.3 part of sulfonated aliphatic polyester as wetting agents. Frequently additional wetting agent and/or oil will be added to the tank mix for postemergence application to facilitate dispersion on the foliage and absorption by the plant.

Other useful formulations for herbicidal applications are emulsifiable concentrates (ECs) which are homogeneous liquid compositions dispersible in water or other dispersant, and may consist entirely of the herbicidal compound and a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone, or other non-volatile organic solvent. For herbicidal application these concentrates are dispersed in water or other liquid carrier, and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied,

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but in general comprises 0.5 to 95% of active ingredient by weight of the herbicidal composition.

Flowable formulations are similar to ECs except that the active ingredient is suspended in a liquid carrier, generally water. Flowables, like ECs, may include a small amount of a surfactant, and contain active ingredient in the range of 0.5 to 95%, frequently from 10 to 50%, by weight of the composition. For application, flowables may be diluted in water or other liquid vehicle, and are normally applied as a spray to the area to be treated.

Typical wetting, dispersing, or emulsifying agents used in agricultural formulations include, but are not limited to, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; alkylaryl polyether alcohols; sulfated higher alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition products of such esters; and the addition product of long-chain mercaptans and ethylene oxide. Many other types of useful surface-active agents are available in commerce. The surface-active agent, when used, normally comprises from 1 to 15% by weight of the composition.

Other useful formulations include suspensions of the active ingredient in a relatively non-volatile liquid such as water, corn oil, kerosene, propylene glycol, or other suitable liquid carrier.

Still other useful formulations for herbicidal applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene, or other organic solvents. Granular formulations, wherein the toxicant is carried on relatively coarse particles, are of

particular utility for aerial distribution or for penetration of cover crop canopy. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freon fluorinated hydrocarbons, may also be used. Water-soluble or water-dispersible granules are also useful formulations for herbicidal application of the present compounds. Such granular formulations are free-flowing, non-dusty, and readily water-soluble or water-miscible. The soluble or dispersible granular formulations described in U.S. patent No. 3,920,442 are useful with the present herbicidal compounds. In use by the farmer on the field, the granular formulations, emulsifiable concentrates, flowable concentrates, solutions, etc., may be diluted with water to give a concentration of active ingredient in the range of say 0.1% or 0.2% to 1.5% or 2%.

The active herbicidal compounds of this invention may be formulated and/or applied with insecticides, fungicides, nematicides, plant growth regulators, fertilizers, or other agricultural chemicals and may be used as effective soil sterilants as well as selective herbicides in agriculture. In applying an active compound of this invention, whether formulated alone or with other agricultural chemicals, an effective amount and concentration of the active compound is of course employed; the amount may be as low as, e.g. about 10 to 100 g/ha, preferably about 30 to 60 g/ha. For field use, where there are losses of herbicide, higher application rates (e.g., four times the greenhouse testing rates mentioned above) may be employed.

The active herbicidal compounds of this invention may be used in combination with other herbicides, e.g., they may be mixed with, say, a lesser, equal, or larger amount of a known herbicide such as aryloxyalkanoic acid herbicides such as (2,4-dichlorophenoxy)acetic acid (2,4-D), (4-chloro-

2-methoxyphenoxy)acetic acid (MCPA), (+/-)-2-(4-chloro-2-methylphenoxy)propanoic acid (MCPP); urea herbicides, such as N,N-dimethyl-N' [4-(1-methylethyl)phenyl]urea (isoproturon); imidazolinone herbicides, such as 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid (imazapyr), a reaction product comprising (+/-)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-4-methylbenzoic acid and (+/-)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methylbenzoic acid (imazamethabenz), (+/-)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid (imazethapyr), and (+/-)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid (imazaquin); diphenyl ether herbicides, such as 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid (aci fluorfen), methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate (bifenox), and 5-[2-chloro-4-(trifluoromethyl)phenoxy]-N-(methylsulfonyl)-2-nitrobenzamide (fomasafen); hydroxybenzonitrile herbicides, such as 4-hydroxy-3,5-diiodobenzonitrile (ioxynil), and 3,5-dibromo-4-hydroxybenzonitrile (bromoxynil); sulfonylurea herbicides, such as 2-[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-benzoic acid (chlormuron), 2-chloro-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide (chlorsulfuron), 2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]benzoic acid (bensulfuron), 2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazol-4-carboxylic acid (pyrazosulfuron), 3-[[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid (thifensulfuron), and 2-(2-chloroethoxy)-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide (triasulfuron); 2-(4-aryloxyphenoxy)alkanoic acid herbicides, such as (+/-)-2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoic acid (fenoxaprop), (+/-)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid (fluazifop), (+/-)-2-[4-(6-chloro-2-quinoxalinyloxy)phenoxy]propanoic acid (quizalofop), and (+/-)-2-[-(2,4-dichlorophenoxy)phenoxy]propanoic acid (diclofop); benzothiadiazinone herbicides, such as 3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide (bentazone); 2-chloroacetanilide herbicides, such as N-(butoxymethyl)-2-chloro-2',6'-diethylacetanilide (butachlor); arencarboxylic acid herbicides, such as 3,6-dichloro-2-

methoxybenzoic acid (dicamba); and pyridyloxyacetic acid herbicides, such as [(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid (fluroxypyr).

One use of the active herbicides of this invention is in combination with grass-controlling herbicides, such as glyphosate, sephoxydim,

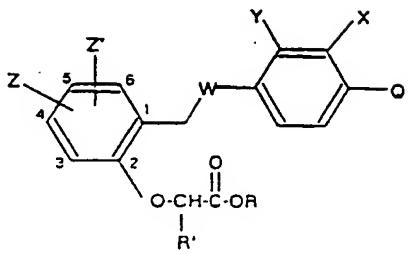
5 quizalofop, or fluazifop. For example, the postemergence application of combinations of Compound 90 of this invention, 2-[2-[4-(1-methyl-6-trifluoromethyl-2,4-(1H,3H)-pyrimidinedione-3-yl)phenoxy]methyl]-5-ethylphenoxy]propionate, with glyphosate have given better control of several weed species, including velvetleaf, morningglory, yellow nutsedge, 10 and barnyardgrass, than either component alone. Such combinations may advantageously applied for control of undesired plants in corn, soybeans, cereals, vineyards and orchards.

15 The active herbicides of this invention may also be used in combination with other herbicide such as 2,4-D or clethodim for enhanced control of broadleaves.

It is apparent that various modifications may be made in the formulation and application of the compounds of this invention without departing from the inventive concepts herein as defined in the claims.

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TABLE 1

 $\text{R}' = \text{CH}_3, \text{W} = \text{O}$

Compound No.	<u>Q</u> ^a	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>Z'</u>	<u>R</u>
1	A	H	H	H	H	CH_3
2	A	F	H	H	H	H
3	A	F	H	H	H	CH_3
4	A	F	H	4-F	H	CH_3
5	A	F	H	3-Cl	H	CH_3
6	A	F	H	4-Cl	H	H
7	A	F	H	4-Cl	H	CH_3
8	A	F	H	5-Cl	H	CH_3
9	A	F	H	4-Br	H	CH_3
10	A	F	H	3-F	4-F	CH_3
11	A	F	H	3-Cl	4-Cl	CH_3
12	A	F	H	4-CH ₃	H	CH_3
13	A	F	H	5-OCH ₃	H	CH_3
14	A	Cl	H	H	H	CH_3
15	A	Cl	H	H	$\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$	
16	A	Cl	H	4-F	H	CH_3
17	A	Cl	H	3-Cl	H	CH_3

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<u>Compound No.</u>	<u>Q^a</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>Z'</u>	<u>R</u>
18	A	Cl	H	4-Cl	H	CH ₃
19	A	Cl	H	4-Br	H	CH ₃
20	A	Cl	H	3-F	4-F	CH ₃
21	A	Cl	H	3-Cl	4-Cl	CH ₃
22	A	Cl	H	4-CH ₃	H	CH ₃
23	B	H	H	H	H	CH ₃
24	B	F	H	H	H	CH ₃
25	B	F	H	4-F	H	CH ₃
26	B	F	H	3-Cl	H	CH ₃
27	B	F	H	4-Cl	H	CH ₃
28	B	F	H	5-Cl	H	CH ₃
29	B	F	H	4-Br	H	CH ₃
30	B	F	H	3-F	4-F	CH ₃
31	B	F	H	3-Cl	4-Cl	CH ₃
32	B	F	H	4-CH ₃	H	CH ₃
33	B	Cl	H	4-F	H	CH ₃
34	B	Cl	H	3-Cl	H	CH ₃
35	B	Cl	H	4-Cl	H	CH ₃
36	B	Cl	H	4-Br	H	CH ₃
37	B	Cl	H	3-Cl	4-Cl	CH ₃
38	B	Cl	H	4-CH ₃	H	CH ₃
39	B	3-OC(CH ₃) ₂ CH ₂ -2	H	H	H	CH ₃

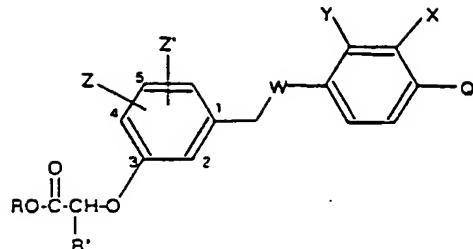
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<u>Compound No.</u>	<u>Q^a</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>Z'</u>	<u>R</u>
40	B	3-OC(CH ₃) ₂ CH ₂ -2		4-Cl	H	CH ₃
41	C	F	H	H	H	CH ₃
42	C	F	H	4-F	H	CH ₃
43	C	F	H	3-Cl	H	CH ₃
44	C	F	H	4-Cl	H	CH ₃
45	C	F	H	3-Cl	4-Cl	CH ₃
46	A	F	H	4-Cl	6-Cl	CH ₃
47	A	F	H	4-CH ₃	H	H
48	A	F	H	4-CH ₃	H	C ₂ H ₅
49	A	F	H	4-CH ₃	H	i-C ₃ H ₇
50	A	F	H	4-C ₂ H ₅	H	H
51	A	F	H	4-C ₂ H ₅	H	CH ₃
52	A	F	H	4-C ₃ H ₇	H	CH ₃
53	A	F	H	4-i-C ₃ H ₇	H	CH ₃
54	A	F	H	4-C ₄ H ₉	H	CH ₃
55	A	F	H	4-t-C ₄ H ₉	H	CH ₃
56	A	F	H	4-C ₂ H ₅	H	CH ₃ OCH ₂ CH(CH ₃)
57	A	F	H	4-CH ₃	H	CH ₃ O(CH ₂) ₂ O(CH ₂) ₂
58	A	F	H	4-C ₂ H ₅	H	CH ₃ O(CH ₂) ₂ O(CH ₂) ₂
59	A	F	H	4-t-C ₄ H ₉	H	CH ₃ O(CH ₂) ₂ O(CH ₂) ₂
60	A	F	H	4-φ	H	CH ₃

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<u>Compound No.</u>	<u>Q^a</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>Z'</u>	<u>R</u>
61	A	F	H	3-(CH ₂) ₄ -4		CH ₃
62	A	Cl	H	4-C ₂ H ₅	H	CH ₃
63	D	F	H	4-Cl	H	CH ₃
64	D	F	H	4-CH ₃	H	CH ₃
65	D	F	H	4-C ₂ H ₅	H	CH ₃
66	E	F	H	4-Cl	H	CH ₃
67	E	F	H	4-CH ₃	H	CH ₃
68	F	F	H	4-CH ₃	H	CH ₃
69	G	F	H	4-Cl	H	CH ₃
70	G	F	H	4-CH ₃	H	CH ₃
71	G	F	H	4-C ₃ H ₇	H	CH ₃
R'=CH ₃ , W=S						
72	A	F	H	4-Cl	H	CH ₃
73	A	F	H	4-CH ₃	H	CH ₃
R'=H, W=O						
74	A	F	H	H	H	CH ₃
75	A	F	H	4-CH ₃	H	CH ₃
76	A	F	H	4-CH ₃	H	H
77	B	F	H	H	H	CH ₃
78	D	F	H	4-CH ₃	H	CH ₃

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 $R' = \text{CH}_3, W = \text{O}$

Compound

No.Q^aXYZZ'R

79

A

F

H

H

H

H

80

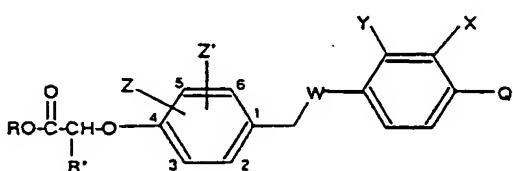
A

F

H

H

H

 CH_3  $R' = \text{CH}_3, W = \text{O}$

Compound

No.Q^aXYZZ'R

81

A

F

H

H

H

 CH_3

82

A

F

H

H

H

 $\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$

83

A

Cl

H

H

H

 CH_3

84

B

F

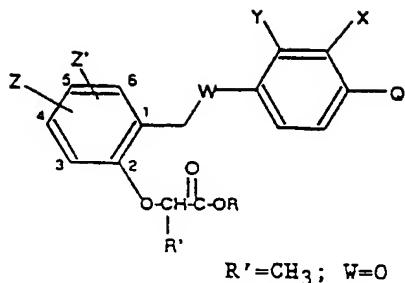
H

H

H

 CH_3

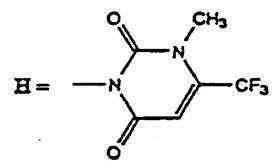
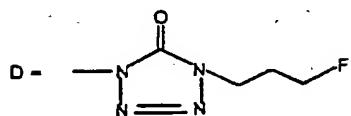
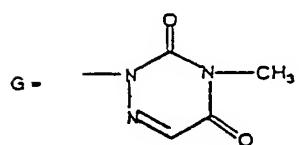
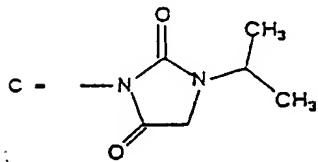
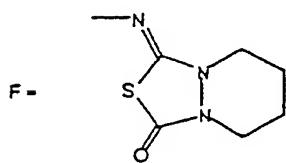
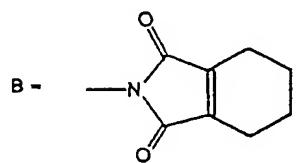
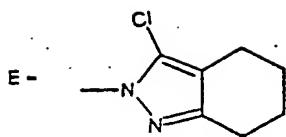
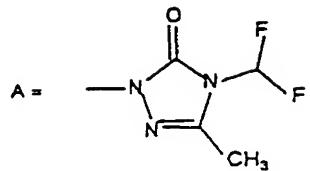
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<u>Compound No.</u>	<u>Q^a</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>Z'</u>	<u>R</u>
85	H	H	H	H	H	CH ₃
86	H	H	H	4-Cl	H	CH ₃
87	H	H	H	4-CH ₃	H	CH ₃
88	H	H	H	4-CH ₃	H	i-C ₃ H ₇
89	H	H	H	4-CH ₃	H	CH ₃ O(CH ₂) ₂ O(CH ₂) ₂
90	H	H	H	4-C ₂ H ₅	H	CH ₃
91	H	H	H	4-C ₂ H ₅	H	CH ₃ O(CH ₂) ₂ O(CH ₂) ₂
92	H	H	H	4-C ₃ H ₇	H	CH ₃
93	H	H	H	4-CH ₃ O	H	CH ₃
94	H	F	H	4-Cl	H	CH ₃
95	H	F	H	4-CH ₃	H	CH ₃
96	H	F	H	4-C ₂ H ₅	H	CH ₃
97	H	F	H	4-C ₃ H ₇	H	CH ₃
98	H	Cl	H	4-Cl	H	CH ₃
99	H	Cl	H	4-CH ₃	H	CH ₃
100	H	CH ₃	H	4-Cl	H	CH ₃
101	H	CH ₃	H	4-CH ₃	H	CH ₃
102	H	CH ₃	H	4-C ₂ H ₅	H	CH ₃
103	H	H	H	4-CH ₃	H	CCl ₃ CH ₂
104	H	H	H	4-C ₂ H ₅	H	CCl ₃ CH ₂

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a.



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TABLE 2
Characterizing Data

Compound <u>No.</u>	MP <u>°C</u>	Compound <u>No.</u>	MP <u>°C</u>	Compound <u>No.</u>	MP <u>°C</u>
1	oil	35	109-111	69	glass
2	74-76	36	oil	70	stiff syrup
3	oil	37	oil	71	stiff syrup
4	84-87	38	oil	72	syrup
5	oil	39	oil	73	syrup
6	oil	40	oil	74	94-97
7	oil	41	oil	75	thick yellow liq.
8	86-88	42	oil	76	110-112
9	86-88	43	oil	77	123-125
10	103-105	44	oil	78	syrup
11	94-96	45	oil	79	oil
12	74-76	46	oil	80	oil
13	oil	47	gel	81	83-85
14	oil	48	98-101	82	oil
15	oil	49	oil	83	oil
16	89-92	50	yellow liq.	84	118-119.5
17	oil	51	yellow liq.	85	oil
18	87-89	52	yellow syrup	86	oil
19	89-92	53	oil	87	52-54
20	80-82	54	syrup	88	oil
21	68-70	55	orange oil	89	oil
22	oil	56	yellow oil	90	oil
23	131-133	57	gel	91	oil
24	oil	58	yellow oil	92	75-78
25	83-86	59	yellow oil	93	oil
26	141-143	60	orange oil	94	oil
27	110-112	61	syrup	95	oil
28	102-103	62	yellow liq.	96	oil
29	113-115	63	syrup	97	oil
30	73-76	64	oil	98	oil
31	oil	65	syrup	99	oil
32	81-83	66	syrup	100	oil
33	oil	67	syrup	101	oil
34	116-118	68	syrup	102	oil
				103	oil
				104	oil

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TABLE 3
PREEMERGENCE HERBICIDAL ACTIVITY (% Control)

Compound No.	1	2	3	4
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.25</u>	<u>0.3</u>
<u>Species</u>				
Soybean	0	0	90	80
Wheat	70	80	20	80
Corn	15	15	15	70
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	90	80	90	100
Cocklebur	10	20	70	80
Blackgrass	80	40	70	95
Green foxtail	90	80	100	100
Johnsongrass	80	70	70	95
Compound No.	5	6	7	8
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	10	10	50	0
Wheat	10	50	95	0
Corn	20	85	10	5
Velvetleaf	100	100	100	85
Morningglory	100	100	100	85
Chickweed	100	100	100	90
Cocklebur	70	100	100	0
Blackgrass	90	100	100	0
Green foxtail	100	100	100	10
Johnsongrass	95	80	70	40
Compound No.	9	10	11	12
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	100	10	0	20
Wheat	80	20	10	70
Corn	95	10	10	50
Velvetleaf	100	100	100	100
Morningglory	100	95	100	100
Chickweed	100	100	100	100
Cocklebur	100	40	60	90
Blackgrass	100	70	20	80
Green foxtail	100	100	100	100
Johnsongrass	95	40	90	60

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	13	14*	15	16
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	0	0	0	10
Wheat	0	5	5	10
Corn	5	10	5	15
Velvetleaf	100	85	100	100
Morningglory	60	70	100	100
Chickweed	20	45	90	100
Cocklebur	30	0	5	60
Blackgrass	0	0	0	20
Green foxtail	85	75	50	100
Johnsongrass	10	30	0	60
Compound No.	17	18	19	20
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	10	0	60	0
Wheat	70	10	-	0
Corn	10	30	20	0
Velvetleaf	100	100	100	100
Morningglory	30	90	90	80
Chickweed	40	100	100	50
Cocklebur	20	40	60	0
Blackgrass	80	10	90	10
Green foxtail	90	100	100	100
Johnsongrass	95	90	90	60
Compound No.	21	22	23	24
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.25</u>
<u>Species</u>				
Soybean	0	10	-	5
Wheat	0	60	5	10
Corn	30	50	5	5
Velvetleaf	100	100	30	80
Morningglory	70	90	100	70
Chickweed	20	80	85	95
Cocklebur	20	10	0	20
Blackgrass	10	30	5	90
Green foxtail	95	95	40	30
Johnsongrass	70	50	60	15

*Average of two tests - where average is not a multiple of five, given as next lower multiple of five.

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	25	26	27	28
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	20	0	10	90
Wheat	20	0	0	95
Corn	10	0	15	95
Velvetleaf	100	85	100	50
Morningglory	100	95	100	20
Chickweed	100	-	100	85
Cocklebur	80	10	80	0
Blackgrass	0	40	70	60
Green foxtail	60	20	0	15
Johnsongrass	10	0	40	85
Compound No.	29	30	31	32
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	90	40	10	30
Wheat	0	0	0	0
Corn	20	0	0	0
Velvetleaf	100	100	100	100
Morningglory	100	90	95	100
Chickweed	100	95	10	100
Cocklebur	85	100	20	80
Blackgrass	-	30	10	30
Green foxtail	95	70	0	100
Johnsongrass	80	10	10	10
Compound No.	33	34	35	36
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	0	0	0	0
Wheat	0	0	0	0
Corn	15	0	10	0
Velvetleaf	100	95	100	100
Morningglory	100	90	95	80
Chickweed	100	-	95	100
Cocklebur	10	10	10	20
Blackgrass	0	10	10	10
Green foxtail	70	0	0	10
Johnsongrass	10	0	20	0

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	37	38	39	40
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	0	0	10	10
Wheat	0	0	-	10
Corn	0	0	-	0
Velvetleaf	80	70	0	0
Morningglory	60	20	10	0
Chickweed	0	50	-	100
Cocklebur	0	10	0	10
Blackgrass	0	0	0	0
Green foxtail	10	40	-	0
Johnsongrass	10	10	20	10

Compound No.	41	42	43	44
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	0	0	0	20
Wheat	0	0	0	0
Corn	0	50	30	20
Velvetleaf	-	0	0	80
Morningglory	10	0	0	80
Chickweed	0	0	0	80
Cocklebur	10	20	0	70
Blackgrass	0	0	0	10
Green foxtail	10	0	0	20
Johnsongrass	30	0	20	30

Compound No.	45	46	47	48
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	0	20	30	90
Wheat	0	10	75	90
Corn	0	10	75	90
Velvetleaf	0	100	100	100
Morningglory	-	95	100	100
Chickweed	0	100	100	100
Cocklebur	-	60	75	100
Blackgrass	0	40	95	95
Green foxtail	0	100	100	100
Johnsongrass	0	90	75	90

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	49	50	51	52
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	75	60	80	90
Wheat	85	75	80	20
Corn	75	30	75	60
Velvetleaf	100	100	100	100
Morningglory	100	85	100	100
Chickweed	100	100	100	100
Cocklebur	100	75	85	95
Blackgrass	90	80	80	40
Green foxtail	100	100	100	100
Johnsongrass	100	80	95	90
 <u>Compound No.</u>				
<u>Rate (kg/ha)</u>	<u>53</u>	<u>54</u>	<u>55</u>	<u>56</u>
<u>Species</u>				
Soybean	100	95	70	90
Wheat	80	0	20	50
Corn	40	30	30	40
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	90	50	80	75
Blackgrass	100	20	75	75
Green foxtail	100	95	95	100
Johnsongrass	70	70	75	95
 <u>Compound No.</u>				
<u>Rate (kg/ha)</u>	<u>57</u>	<u>58</u>	<u>59</u>	<u>60</u>
<u>Species</u>				
Soybean	40	60	50	75
Wheat	80	75	20	20
Corn	75	40	20	20
Velvetleaf	100	100	100	100
Morningglory	95	100	85	100
Chickweed	100	100	90	100
Cocklebur	70	30	75	60
Blackgrass	80	75	70	60
Green foxtail	100	100	90	100
Johnsongrass	80	90	80	70

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	61	62	63	64
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	40	40	40	30
Wheat	20	70	10	20
Corn	20	50	10	30
Velvetleaf	100	100	100	100
Morningglory	80	100	100	90
Chickweed	70	100	100	100
Cocklebur	10	60	75	60
Blackgrass	40	85	70	30
Green foxtail	100	100	100	50
Johnsongrass	70	80	75	30
Compound No.	65	66	67	68
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	85	10	10	40
Wheat	10	10	10	10
Corn	10	0	10	10
Velvetleaf	100	80	100	100
Morningglory	100	10	100	90
Chickweed	100	0	60	100
Cocklebur	80	10	30	40
Blackgrass	50	30	60	30
Green foxtail	100	0	75	80
Johnsongrass	80	0	10	40
Compound No.	69	70	71	72
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	60	20	85	40
Wheat	40	40	20	40
Corn	20	50	30	60
Velvetleaf	100	100	100	100
Morningglory	100	100	100	95
Chickweed	100	100	100	100
Cocklebur	90	30	85	75
Blackgrass	40	0	0	75
Green foxtail	100	100	100	90
Johnsongrass	95	20	75	50

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	73	74	75	76
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	0	10	10	20
Wheat	0	80	60	60
Corn	0	20	20	70
Velvetleaf	100	100	100	100
Morningglory	80	100	100	100
Chickweed	100	80	75	80
Cocklebur	20	0	10	30
Blackgrass	70	95	75	60
Green foxtail	100	80	100	100
Johnsongrass	30	70	70	80
Compound No.	77	78	79	80
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	10	10	0	0
Wheat	5	20	10	85
Corn	10	10	20	5
Velvetleaf	10	100	100	100
Morningglory	80	100	95	100
Chickweed	20	30	95	90
Cocklebur	10	60	0	20
Blackgrass	5	30	40	50
Green foxtail	20	80	70	100
Johnsongrass	20	50	95	80
Compound No.	81	82	83	84
Rate (kg/ha)	<u>0.25</u>	<u>0.25</u>	<u>0.3</u>	<u>0.25</u>
<u>Species</u>				
Soybean	0	0	0	10
Wheat	0	5	5	0
Corn	10	40	5	5
Velvetleaf	50	95	0	0
Morningglory	80	85	0	10
Chickweed	15	30	90	5
Cocklebur	20	40	0	5
Blackgrass	60	60	0	0
Green foxtail	95	85	-	30
Johnsongrass	10	80	5	10

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	85	86	87	88
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	60	85	75	90
Wheat	10	30	50	0
Corn	75	75	60	20
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	45	100	70	50
Blackgrass	90	75	60	20
Green foxtail	100	90	95	100
Johnsongrass	90	95	95	30
Compound No.	89	90	91	92
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	100	100	100	95
Wheat	30	90	10	0
Corn	75	90	90	60
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	95	90	95
Blackgrass	95	60	85	40
Green foxtail	100	100	100	100
Johnsongrass	100	100	100	95
Compound No.	93	94	95	96
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	40	100	90	95
Wheat	20	0	10	60
Corn	40	45	85	60
Velvetleaf	100	100	100	100
Morningglory	100	100	95	100
Chickweed	100	100	100	100
Cocklebur	75	100	100	90
Blackgrass	75	85	70	40
Green foxtail	70	100	100	100
Johnsongrass	75	100	95	75

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TABLE 3 (continued)
PREEMERGENCE HERBICIDAL ACTIVITY

Compound No.	97	98	99	100
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	95	10	20	50
Wheat	20	0	0	0
Corn	30	20	20	60
Velvetleaf	100	100	100	100
Morningglory	100	60	20	90
Chickweed	100	100	ND	100
Cocklebur	90	40	40	80
Blackgrass	30	0	20	20
Green foxtail	95	70	100	100
Johnsongrass	60	40	80	80
Compound No.	101	102	103	104
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	70	75	60	100
Wheat	10	0	60	20
Corn	75	10	80	60
Velvetleaf	100	100	100	100
Morningglory	60	60	100	100
Chickweed	100	95	100	100
Cocklebur	60	70	90	80
Blackgrass	30	0	95	80
Green foxtail	95	100	100	100
Johnsongrass	60	100	95	95

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TABLE 4
POSTEMERGENCE HERBICIDAL ACTIVITY (% Control)

<u>Compound No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.25</u>	<u>0.3</u>
<u>Species</u>				
Soybean	60	85	95	95
Wheat	85	100	95	100
Corn	70	100	95	100
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	90	-	100	100
Cocklebur	50	100	100	100
Blackgrass	30	90	95	100
Green foxtail	100	100	100	100
Johnsongrass	80	100	90	100
<u>Compound No.</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	80	90	95	40
Wheat	95	100	100	20
Corn	100	100	100	40
Velvetleaf	100	100	100	70
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	100	40
Blackgrass	40	100	100	0
Green foxtail	100	100	100	70
Johnsongrass	95	100	90	10
<u>Compound No.</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	100	95	80	95
Wheat	100	100	95	100
Corn	100	100	100	100
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	95	100	100
Cocklebur	100	95	100	-
Blackgrass	100	100	95	100
Green foxtail	100	100	100	100
Johnsongrass	100	95	100	100

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TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY (% Control)

Compound No.	13 <u>0.3</u>	14* <u>0.3</u>	15 <u>0.3</u>	16 <u>0.3</u>
<u>Species</u>				
Soybean	70	50	50	75
Wheat	20	50	95	100
Corn	75	75	95	95
Velvetleaf	80	100	100	100
Morningglory	60	100	100	100
Chickweed	0	5	10	100
Cocklebur	60	55	60	100
Blackgrass	5	10	5	60
Green foxtail	20	90	100	100
Johnsongrass	40	35	70	95
Compound No.	17 <u>0.3</u>	18 <u>0.3</u>	19 <u>0.3</u>	20 <u>0.3</u>
<u>Species</u>				
Soybean	60	85	60	70
Wheat	30	100	100	95
Corn	95	100	100	100
Velvetleaf	100	100	100	100
Morningglory	95	100	100	100
Chickweed	20	100	100	80
Cocklebur	80	100	100	90
Blackgrass	10	95	100	70
Green foxtail	30	100	100	100
Johnsongrass	85	100	95	100
Compound No.	21 <u>0.3</u>	22 <u>0.3</u>	23 <u>0.3</u>	24 <u>0.25</u>
<u>Species</u>				
Soybean	30	70	40	90
Wheat	20	100	15	20
Corn	30	90	30	100
Velvetleaf	95	100	80	100
Morningglory	100	100	100	100
Chickweed	20	95	40	100
Cocklebur	80	-	20	100
Blackgrass	20	95	5	60
Green foxtail	95	100	15	85
Johnsongrass	90	70	10	70

*Average of two tests - where average is not a multiple of five, given as next lower multiple of five.

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TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY

Compound No.	25	26	27	28
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	75	60	95	95
Wheat	10	20	15	90
Corn	75	75	100	80
Velvetleaf	100	60	100	90
Morningglory	100	100	100	95
Chickweed	100	20	100	95
Cocklebur	100	100	100	70
Blackgrass	0	0	10	85
Green foxtail	80	0	90	20
Johnsongrass	95	10	50	40
Compound No.	29	30	31	32
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	90	90	40	95
Wheat	30	20	15	10
Corn	80	80	100	80
Velvetleaf	100	100	100	100
Morningglory	100	95	100	100
Chickweed	100	95	30	100
Cocklebur	90	100	85	-
Blackgrass	0	10	0	0
Green foxtail	50	80	80	60
Johnsongrass	0	60	30	20
Compound No.	33	34	35	36
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	70	10	60	40
Wheat	0	10	15	0
Corn	50	25	25	80
Velvetleaf	100	50	100	100
Morningglory	100	90	100	100
Chickweed	80	0	100	95
Cocklebur	80	10	80	95
Blackgrass	10	0	0	0
Green foxtail	20	0	50	30
Johnsongrass	0	0	50	0

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TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY

Compound No.	37	38	39	40
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	30	20	10	0
Wheat	15	0	0	0
Corn	10	60	10	15
Velvetleaf	85	80	10	0
Morningglory	50	100	0	0
Chickweed	10	80	20	0
Cocklebur	60	-	0	0
Blackgrass	10	0	0	0
Green foxtail	10	30	20	0
Johnsongrass	4	0	0	0

Compound No.	41	42	43	44
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	30	70	30	80
Wheat	0	10	0	40
Corn	30	40	0	70
Velvetleaf	100	85	70	100
Morningglory	100	100	85	100
Chickweed	-	70	0	90
Cocklebur	-	90	60	100
Blackgrass	0	0	0	0
Green foxtail	20	30	10	20
Johnsongrass	50	30	30	10

Compound No.	45	46	47	48
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	50	60	80	95
Wheat	0	90	95	100
Corn	40	75	100	100
Velvetleaf	60	100	100	100
Morningglory	80	100	100	100
Chickweed	0	100	100	100
Cocklebur	95	100	100	100
Blackgrass	0	80	100	100
Green foxtail	30	100	100	100
Johnsongrass	70	100	100	100

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TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY

Compound No.	49	50	51	52
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	75	95	100	100
Wheat	95	90	95	100
Corn	50	90	100	100
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	100	100
Blackgrass	100	100	100	85
Green foxtail	100	100	100	100
Johnsongrass	100	100	95	100

Compound No.	53	54	55	56
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	100	100	90	90
Wheat	100	60	70	95
Corn	80	70	50	60
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	95	100
Cocklebur	100	100	100	100
Blackgrass	100	60	90	95
Green foxtail	100	100	100	100
Johnsongrass	100	100	95	100

Compound No.	57	58	59	60
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	80	95	90	100
Wheat	85	100	95	90
Corn	100	100	60	-
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	95	100	100
Blackgrass	95	100	90	75
Green foxtail	100	100	100	100
Johnsongrass	100	100	100	100

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TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY

Compound No.	61	62	63	64
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	95	85	85	75
Wheat	40	90	80	85
Corn	60	80	75	60
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	100	100
Blackgrass	70	95	75	80
Green foxtail	100	100	100	100
Johnsongrass	100	100	95	90

Compound No.	65	66	67	68
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	95	40	40	95
Wheat	90	0	10	20
Corn	70	20	20	60
Velvetleaf	100	95	100	100
Morningglory	100	80	100	100
Chickweed	100	100	95	100
Cocklebur	100	100	100	100
Blackgrass	85	10	10	70
Green foxtail	100	95	80	100
Johnsongrass	100	-	70	95

Compound No.	69	70	71	72
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>

Species

Soybean	80	80	95	60
Wheat	100	100	100	100
Corn	100	100	100	100
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	100	100
Blackgrass	95	80	80	85
Green foxtail	100	100	100	100
Johnsongrass	100	100	100	100

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TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY

Compound No.	73	74	75	76
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	60	50	85	85
Wheat	100	85	50	50
Corn	100	95	80	60
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	90	100	100
Cocklebur	100	90	100	60
Blackgrass	100	95	80	100
Green foxtail	100	90	100	100
Johnsongrass	95	70	95	85
Compound No.	77	78	79	80
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	15	60	70	50
Wheat	20	50	70	85
Corn	50	80	100	100
Velvetleaf	95	100	80	100
Morningglory	100	100	100	100
Chickweed	-	100	0	90
Cocklebur	90	100	90	90
Blackgrass	10	20	15	40
Green foxtail	10	95	70	100
Johnsongrass	20	85	85	90
Compound No.	81	82	83	84
Rate (kg/ha)	<u>0.25</u>	<u>0.25</u>	<u>0.3</u>	<u>0.25</u>
<u>Species</u>				
Soybean	85	70	50	95
Wheat	95	70	15	20
Corn	100	80	70	50
Velvetleaf	100	95	40	30
Morningglory	100	100	40	80
Chickweed	-	90	10	15
Cocklebur	80	85	60	85
Blackgrass	95	90	5	0
Green foxtail	100	100	85	60
Johnsongrass	85	80	40	50

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TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY

Compound No.	85	86	87	88
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	95	100	95	80
Wheat	45	90	40	85
Corn	100	85	75	100
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	80	100
Blackgrass	75	95	90	90
Green foxtail	100	90	95	100
Johnsongrass	100	95	95	100
Compound No.	89	90	91	92
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	95	100	100	100
Wheat	95	95	100	40
Corn	100	100	100	75
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	ND	100
Blackgrass	100	100	80	90
Green foxtail	100	100	100	100
Johnsongrass	100	100	100	100
Compound No.	93	94	95	96
<u>Rate (kg/ha)</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	90	100	100	100
Wheat	100	85	90	95
Corn	100	75	95	100
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	95	100
Blackgrass	100	100	100	95
Green foxtail	100	90	100	100
Johnsongrass	100	100	100	100

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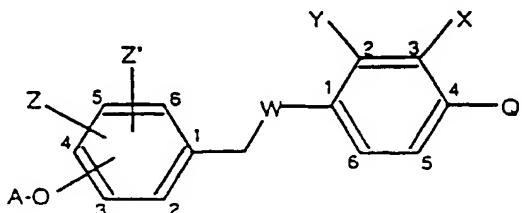
TABLE 4 (continued)
POSTEMERGENCE HERBICIDAL ACTIVITY

Compound No.	97	98	99	100
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	100	85	60	90
Wheat	ND	40	40	30
Corn	80	70	70	95
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	100	100	100
Blackgrass	80	30	30	70
Green foxtail	90	90	70	80
Johnsongrass	95	90	70	95
Compound No.	101	102	103	104
Rate (kg/ha)	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>0.3</u>
<u>Species</u>				
Soybean	80	90	95	100
Wheat	10	70	100	90
Corn	90	80	95	100
Velvetleaf	100	100	100	100
Morningglory	100	100	100	100
Chickweed	100	100	100	100
Cocklebur	100	85	100	100
Blackgrass	40	80	60	20
Green foxtail	90	100	100	100
Johnsongrass	100	100	100	100

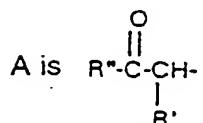
I claim:

1. A herbicidal composition comprising a herbicidally effective amount of a mixture of a compound of the formula

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10 in which



Q is 1-methyl-6-trifluoromethyl-2,4-(1H,3H)pyrimidinedione-3-yl;

15 R is hydrogen, M, lower alkyl, cycloalkyl, lower alkenyl, or lower alkynyl, each optionally substituted with one or more chlorine or fluorine, or $-\text{[CHR}^7\text{-(CH}_2\text{)}_m\text{O}]_n\text{R}^8$;

R' is hydrogen or methyl;

20 R'' is -OR or amino, phenylamino, lower alkyl amino, lower alkenylamino, lower alkoxyamino, cyano, or lower alkyl-, lower haloalkyl-, or phenylsulfonylamino of the formula $-\text{N(lower alkyl)-SO}_2\text{R}^9$ or $-\text{NHSO}_2\text{R}^9$;

R⁷ is H or CH₃;

R⁸ is lower alkyl;

R⁹ is lower alkyl, lower haloalkyl, or phenyl;

25 X is hydrogen, methyl, fluorine, or chlorine;

Y is hydrogen;

W is oxygen or sulfur;

Z is hydrogen, fluorine, chlorine, bromine, lower alkyl, or methoxy;

Z' is hydrogen, fluorine, or chlorine;

30 m is 0 to 2, and n is 0 to 6;

M is sodium, potassium, or ammonium; and

the group AO- may be in the 2, 3, or 4 position of the phenyl ring, and a herbicide having a different structure in admixture with a suitable carrier.

2. A composition of claim 1 in which R" is -OR; X is hydrogen, fluorine, or chlorine; and Z is hydrogen, chlorine, or lower alkyl;
3. A composition of claim 2 in which R is lower alkyl, lower chloroalkyl, or -[CHR⁷-(CH₂)_mO]_nR⁸;
- 5 R' is methyl;
Z is in the 4-position;
Z' is hydrogen or chlorine in the 3-position;
m is 0 or 1, n is 1 to 3; and
the group AO- is in the 2-position of the phenyl ring.
- 10 4. A composition of claim 3 in which R is methyl, 2,2,2-trichloroethyl, or CH₃O(CH₂)-O-(CH₂)₂-; X is hydrogen or fluorine; W is oxygen, and Z' is hydrogen, and the herbicide of different structure is a grass-controlling herbicide.
- 15 5. The composition of claim 4 in which R and Z are each methyl, and X is hydrogen.
6. The composition of claim 4 in which R is methyl, and X is hydrogen, and Z is ethyl.
7. The composition of claim 4 in which R and Z are each methyl, and X is fluorine.
- 20 8. The composition of claim 4 in which R is methyl, and X is fluorine, and Z is ethyl.
9. The composition of claim 4 in which R is 2,2,2-trichloroethyl, X is hydrogen, and Z is methyl.
10. The composition of claim 4 in which R is 2,2,2-trichloroethyl, X is 25 hydrogen, and Z is ethyl.
11. The composition of claim 4 in which R is methyl, X is hydrogen, and Z is ethyl.
12. A composition of claim 4 in which the grass-controlling herbicide is glyphosate, sephoxydim, quizalofop, or fluazifop .
- 30 13. A composition of claim 3 in which Q is 1-methyl-6-trifluoromethyl-2,4-(1H,3H)pyrimidinedione-3-yl; R is methyl, 2,2,2-trichloroethyl, or CH₃O(CH₂)-O-(CH₂)₂-; X is hydrogen or fluorine; W is oxygen, and Z' is hydrogen, and the herbicide of different structure is a broadleaf herbicide.
14. A composition of claim 13 in which the broadleaf herbicide is 2,4-D or 35 clethodim.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/14193

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N43/54 C07D239/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 262 390 (G. THEODORIDIS) 16 November 1993 see column 2, line 14 - column 3, line 44 see column 36, line 17 -----	1-14

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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1

Date of the actual completion of the international search 17 January 1997	Date of mailing of the international search report 30.01.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer Decorte, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/14193

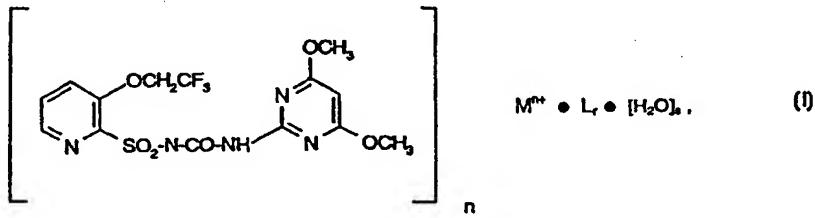
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ :	A1	(11) International Publication Number: WO 00/52006 (43) International Publication Date: 8 September 2000 (08.09.00)
C07D 401/12, A01N 47/36		
(21) International Application Number:	PCT/EP00/01627	Andreas [CH/CH]; Blotzheimerstrasse 29, CH-4055 Basel (CH).
(22) International Filing Date:	28 February 2000 (28.02.00)	(74) Agent: BECKER, Konrad; Novartis AG, Corporate Intellectual Property, Patent & Trademark Dept., CH-4002 Basel (CH).
(30) Priority Data:	369/99 1 March 1999 (01.03.99) CH	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
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(54) Title: SULFONYLUREA SALTS AS HERBICIDES



(57) Abstract

Compounds of formula (I) wherein M is an alkali metal or an alkaline earth metal; n is 1 or 2; r and s, independently of one another, are 0, 1/2, 1, 1.5, 2, 2.5 or 3; and L is ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, methylene chloride, trichloromethane, trichloroethane, tetrahydrofuran, diethylether, 1, 2-dimethoxyethane, dioxane, methyl-tert.-butylether, chlorobenzene, toluene or xylene, with the provision that r is other than 1.5 if L is dioxane and s is 0, are suitable for use as herbicides.

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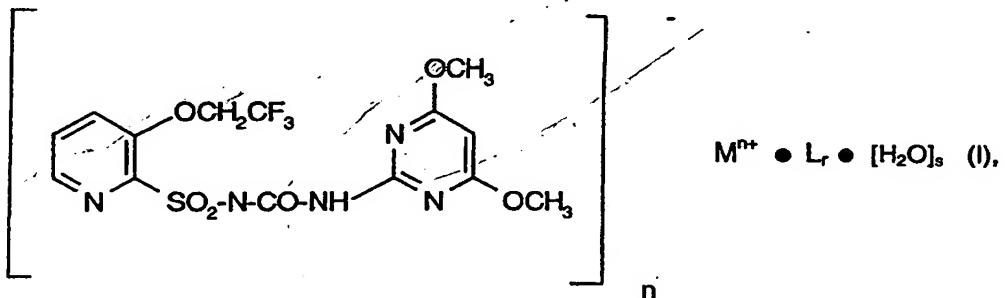
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be falsified by the presence of amorphous material and by the evaporation of solvatising solvent.

It is therefore the aim of the present invention to specifically provide crystal modifications of salts of N-[3-(2-trifluoroethoxy)-pyridin-2-yl-sulfonyl]-N'-(4,6-dimethoxy-pyrimidin-2-yl)-urea, the properties of which substantially improve the technical preparation of the active ingredient, its formulation and its storability.

Accordingly, the present invention relates to compounds of formula I



wherein

M is an alkali metal or an alkaline earth metal;

n is 1 or 2;

r and s, independently of one another, are 0, ½, 1, 1½, 2, 2½ or 3; and

L is ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, methylene chloride, trichloromethane, trichloroethane, tetrahydrofuran, diethylether, 1,2-dimethoxyethane, dioxane, methyl-tert.-butylether, chlorobenzene, toluene or xylene, with the provision that r is other than 1½ if L is dioxane and s is 0.

M as an alkali metal and as an alkaline earth metal in the context of the present invention is preferably sodium, potassium, magnesium and calcium.

The present invention includes all crystal modifications that may be formed by the compounds of formula I.

Preferred compounds of formula I are characterised in that L is dioxane, tetrahydrofuran or water.

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SULFONYLUREA SALTS AS HERBICIDES

The present invention relates to novel herbicidally active pyridylsulfonlurea salts, to processes for their preparation, to compositions comprising said compounds, and to the use thereof for controlling weeds, in particular in crops of cultivated plants or for inhibiting plant growth.

Various crystal forms (modifications) of a chemical compound can exhibit very different physical properties, which may lead to unforeseeable problems during technical preparation and processing of these compounds.

The characteristics of crystal modifications frequently have a crucial influence on the separating ability (filtration), stirrability (crystal volume), surface activity (foaming), rate of drying, solubility, quality, formulating ability and storage stability (e.g. hygroscopy) of for example pharmaceutically and agronomically active compounds. For example, the grinding and formulating properties (e.g. tabletting) of products may be completely different, depending on the respective crystal modification (Pharm. Ind. 59, 2, 165-169 (1997)). Since, in the various stages of synthesis of a preparation process, different physical properties of the respective synthesis products are of importance, it is especially advantageous to find the optimally suited crystal form for the respective stage of synthesis.

Furthermore, a modification can suddenly transform into another undesired modification under certain thermodynamic conditions. These transformations may be reversible or irreversible and are generally not predictable.

Pyridylsulfonlurea salts with herbicidal activity are described for example in WO 97/41112. From the description of the preparation of the sodium salt of N-[3-(2-trifluoroethoxy)-pyridin-2-yl-sulfonyl]-N'-(4,6-dimethoxy-pyrimidin-2-yl)-urea mentioned in this document, however, it is not possible to deduce whether amorphous or crystalline products are obtained, or which crystal modification or mixtures of modifications are produced, since physical parameters such as temperature, humidity and pressure which are crucial for targeted synthesis are not mentioned. In addition, the melting point only characterises a crystal structure insufficiently, since during the measuring procedure the original crystal modification can be transformed into another modification or into mixtures of modifications. Moreover, the melting point may

Further preference is given to compounds of formula I, in which n is 1, and M is especially sodium.

Also preferred are compounds of formula I, in which M is sodium, n is 1, r is 0 and s is 0.

Also notable is the amorphous solid form of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0. For example, this form can be used to produce other crystal modifications, such as the C-modification. The amorphous form therefore forms a further object of the present invention.

Particularly preferred individual compounds falling within the scope of formula I are the compounds selected from

- the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 10.0/average; 9.2/strong; 8.6/very weak; 8.1/weak; 7.2/strong; 6.9/strong; 6.4/average; 5.82/strong; 5.75/strong; 5.64/very strong; 5.53/very weak; 5.13/average; 4.97/very strong; 4.65/average; 4.30/very strong; 4.22/weak; 4.15/very weak; 4.02/weak; 3.94/weak; 3.79/average; 3.73/weak; 3.68/average; 3.61/weak; 3.58/weak; 3.52/very strong; 3.42/very weak; 3.37/weak; 3.31/very weak; 3.27/very weak; 3.23/weak; 3.18/average; 3.08/very weak; 3.03/very weak; 2.95/very weak; 2.87/strong; 2.82/very weak; 2.79/very weak; 2.73/very weak; 2.68/very weak; 2.65/very weak; 2.63/very weak; 2.60/weak; 2.57/weak;
- the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0. characterised by the X-ray powder pattern with d[Å]/intensity: 15.7/weak; 10.2/very strong; 8.2/weak; 7.8/weak; 7.3/weak; 6.7/weak; 6.5/very weak; 6.2/average; 5.64/very weak; 5.53/weak; 5.42/weak; 5.09/weak; 4.96/average; 4.86/very weak; 4.60/average; 4.37/average; 4.24/weak; 4.11/very strong; 3.95/very weak; 3.90/weak; 3.81/very weak; 3.71/average; 3.62/weak; 3.52/very weak; 3.43/strong; 3.37/weak; 3.32/very weak; 3.27/weak; 2.94/very weak; 2.82/average;
- the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, characterised by the X-ray powder pattern with d[Å]/intensity: 13.4/weak; 10.1/very

weak; 9.3/very strong; 7.8/weak; 6.9/very weak; 6.7/very weak; 5.63/very weak; 5.35/average; 4.66/weak; 4.44/very weak; 4.35/weak; 4.12/strong; 3.94/strong; 3.87/very weak; 3.76/weak; 3.61/average; 3.49/very weak; 3.40/very weak;

- the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 13.1/average; 11.0/very strong; 8.8/weak; 7.7/very strong; 7.2/very strong; 7.0/weak; 6.4/weak; 6.2/strong; 5.96/weak; 5.90/weak; 5.64/strong; 5.47/weak; 5.34/average; 5.19/weak; 4.79/weak; 4.74/average; 4.64/very weak; 4.55/strong; 4.47/weak; 4.35/strong; 4.26/average; 4.13/weak; 4.06/very weak; 3.92/very strong; 3.87/weak; 3.79/very strong; 3.67/weak; 3.61/average; 3.58/strong; 3.47/weak; 3.32/very weak; 3.24/average; 3.14/weak; 3.12/weak; 3.07/weak; 3.04/strong; 2.97/very weak; 2.92/very weak; 2.88/weak; 2.82/weak; 2.77/very weak; 2.74/very weak; 2.69/weak; 2.66/very weak; and

- the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 1.6/weak; 9.8/very weak; 8.0/very strong; 7.6/average; 6.7/strong; 6.4/very weak; 6.3/weak; 6.1/very weak; 5.80/average; 5.66/very weak; 5.47/strong; 5.12/very weak; 5.08/very weak; 4.84/weak; 4.76/weak; 4.47/strong; 4.40/weak; 4.21/average; 4.19/average; 4.15/very weak; 4.00/very weak; 3.93/very weak; 3.84/average; 3.72/very strong; 3.58/average; 3.52/average; 3.32/very weak; 3.28/very weak; 3.25/very weak; 3.11/very weak; 3.07/very weak; 2.95/very weak; 2.86/weak; 2.82/very weak; 2.75/very weak; 2.57/weak; 2.49/very weak.

Special significance is attributed to the B-modification.

Preference is also given to

- the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, produced by drying the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification), at a temperature of 35°C to 65°C in a vacuum.

- the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, produced either by

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contact of the essentially amorphous form (A-modification) by air of 98% relative humidity or mixing the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, with water in a ratio of water to K-modification of 0.1 : 1 to 0.4 : 1 and separating and drying the product obtained at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;

- the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, produced by adding water to the compound of formula I, in which M is sodium, n is 1, and L, r and s are defined as for formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, filtering and drying the residue of filtration at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars, or preferably produced by adding water to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (K-modification), or to the compound of formula I, in which M is sodium; n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification) or to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1 (I-modification), or to the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1 (C-modification), in a ratio of water to the K, J, I or C modification of 0.5 : 1 to 20 : 1, filtering and drying the residue of filtration at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

In the K-modification, the surprisingly high thermodynamic stability and the non-hygroscopic properties are especially notable. The B-modification similarly has high stability in the presence of water. This property is of advantage especially in the preparation of formulations of the active ingredient. Particular importance is therefore placed on the K and B modifications.

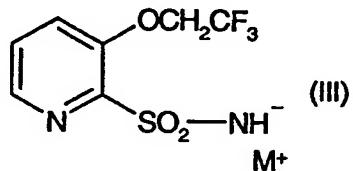
The compounds of formula I may be produced by a generally known process, whereby a compound of formula II



in ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, methylene chloride, trichloromethane,

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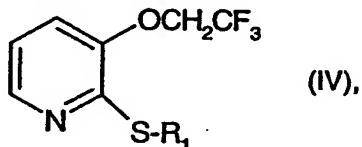
trichloroethane, tetrahydrofuran, diethylether, 1,2-dimethoxyethane, dioxane, methyl-tert.-butylether, chlorobenzene, toluene or xylene, is reacted with a compound of formula III



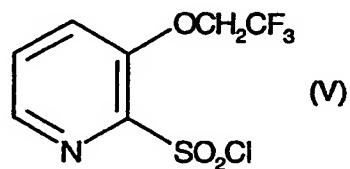
wherein M is as defined under formula I.

The compound of formula II is reacted with the compound of formula III at temperatures of -20°C to 180°C, a temperature range of 30–80°C being preferred. The compounds of formulae II and III can be used in equivalent stoichiometric quantities, although a slight excess of isocyanate may be of advantage.

The preparation of the starting compound of formula II is described, for example, in EP-A-0 232 067, page 29. The compounds of formula III may be prepared, for example, by converting the compound of formula IV



wherein R₁ is -CH₂-phenyl or isopropyl, by means of aqueous chlorination, into the compound of formula V



This compound is treated with aqueous ammonia, and the resulting sulfonamide is then reacted with 30% sodium methylate. Such reactions are known, and are familiar to the specialist.

Preferred crystal modifications of the compounds of formula I are produced by processes that have been specially developed for the present invention. These processes therefore form a further object of the present invention.

The process for the preparation of the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0, is thus characterised in that a 5-25% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran.

After adding the 4,6-dimethoxy-pyrimidine-2-isocyanate, the reaction mixture is stirred until conversion is complete. This process is preferably carried out at a temperature of 40-50°C. The J-modification obtained can be separated from the reaction mixture by filtration.

The process for the preparation of the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, is characterised in that a 5-25% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, then filtered, and the residue of filtration (J-modification) is subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

After adding the 4,6-dimethoxy-pyrimidine-2-isocyanate, the reaction mixture is stirred until conversion is complete. For drying in this process variant, a temperature of 40-60°C and a pressure of 0.02 to 0.06 bars are preferred.

The process for the production of the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, is characterised in that either the essentially amorphous form (A-modification) is exposed to an atmosphere of 98% relative humidity, or the K-modification is mixed with water in a ratio of water to K-modification of 0.1 : 1 to 0.4 : 1, then filtered, and the residue of filtration subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

When producing the C-modification, the ratio of water to K-modification may vary from 0.1 : 1 to 0.4 : 1, a ratio of 0.1 : 1 to 0.3 : 1 being preferred in particular. The addition of water may take place at a temperature of 0-60°C, most preferably at a temperature of 5-40°

C. Drying of the C-modification is preferably effected at a temperature of 40-60°C and at a pressure of 0.02-0.06 bars.

The C-modification may be advantageously produced whereby N-[(4,6-dimethoxy-2-pyrimidinyl)carbamoyl]-3-(2,2,2-trifluoro-ethoxy)-pyridine-2-sulfonamide is added to a solution of aqueous sodium hydroxide, afterwards it is concentrated by evaporation under vacuum at a temperature of 50°C, the residue thus obtained is stirred up with diethyl ether, filtered, dried at temperatures of $\geq 120^\circ\text{C}$ and the essentially amorphous salt thus obtained (A-modification) is then exposed to an atmosphere of 98% relative humidity.

The process for the preparation of the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, is characterised in that a 5-25% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 0-30°C to a 10-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, and subsequently 1-20 molar equivalents of water, based on the 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt, are added.

In this variant, the addition of 2-5 molar equivalents of water is preferred in particular.

The process for the production of the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, is characterised in that water is added to the compound of formula I, in which M is sodium, n is 1 and L, r and s are defined as in formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, then filtration takes place and the residue of filtration is dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

A preferred variant of the process according to the invention for the production of the B-modification is characterised in that water is added to the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (K-modification), or to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is $\frac{1}{2}$ and s is 0 (J-modification) or to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1 (I-modification), or to the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1 (C-modification), in a ratio of water to the K, J, I or C modification of 0.5 : 1 to 20 : 1, then

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filtration takes place and the residue of filtration is subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

The temperature during the water addition may vary from 0-80°C. A temperature of 5-40°C is preferred in particular. The residue of filtration may be dried at temperatures of 30-90°C and at a pressure of 0.01 to 0.1 bars, preferably at a temperature of 40-60°C and at a pressure of 0.02-0.06 bars. It is most advantageous to mix the suspension with seed crystals of the B-modification in order to accelerate crystal growth.

The compounds of formula I may be used as herbicides in unmodified form, i.e. as obtained in the synthesis. However, they are preferably processed in conventional manner with the excipients that are customary in formulation technology, e.g. into directly sprayable or dilutable solutions, wettable powders, soluble or dispersible powders, soluble or dispersible granulates, dusts, and also so-called non-aqueous flowables. A composition which is especially preferred according to the invention is present in the form of soluble or dispersible granulates and contains crystal modification B as the compound of formula I.

Suitable formulations for the compounds of formula I are described for example in WO 97/34485 on pages 9 to 13. As with the type of agents, the methods of application such as spraying, atomising, dusting, wetting, scattering or pouring, are selected in accordance with the intended objectives and the prevailing circumstances.

The formulations, i.e. the agents, preparations, or compositions containing the active ingredient of formula I or at least one active ingredient of formula I and usually one or more solid or liquid formulation assistants, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredients with said formulation auxiliaries, typically solvents or solid carriers. Surface-active compounds (surfactants) may additionally be used for preparing the formulations. Examples of solvents and solid carriers are described in WO 97/34485 on page 6.

Depending on the type of active ingredient of formula I to be formulated, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants and surfactant mixtures having good dispersing and wetting properties.

Examples of suitable anionic, nonionic, and cationic surfactants are listed for example in WO 97/34485 on pages 7 and 8.

Also the surfactants customarily for the art of formulation and described, *inter alia*, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch" (Handbook of Surfactants), Carl Hanser Verlag, Munich/Vienna, 1981, and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81 are suitable for manufacture of the herbicides according to the invention.

The herbicidal formulations will as a rule contain from 0.1 to 99 % by weight, preferably from 0.1 to 95% by weight, of herbicide, from 1 to 99.9% by weight, preferably from 5 to 99.8 % by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant. Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations. The compositions may also contain further ingredients, such as stabilisers, e.g. where appropriate epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil, or soybean oil), antifoams, typically silicone oil, preservatives, viscosity regulators, binders, and tackifiers, as well as fertilisers or other chemical agents.

The compounds of formula I are usually applied with success to the plants or the locus thereof in concentrations of 0.001 to 0.5 kg/ha, preferably 0.005 to 0.25 kg/ha. The concentration required to achieve the desired action can be determined by experimentation. It will depend on the type of action, the development stage of the cultivated plant and of the weed, as well as on the application (locus, time, method), and as a result of these variables can vary over a wide range.

The compounds of formula I have excellent herbicidal and growth inhibiting properties, which make them suitable for application in crops of cultivated plants, especially in cereals, cotton, soybeans, sugar beet, sugar cane, plantations, rape, maize, and rice, and for the non-selective control of weeds. Crops will also be understood to mean those crops that have been made tolerant to herbicides or classes of herbicides by conventional breeding or genetic engineering methods. The weeds to be controlled may be monocot as well as dicot

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weeds, typically *Stellaria*, *Nasturtium*, *Agrostis*, *Digitaria*, *Avena*, *Setaria*, *Sinapis*, *Lolium*, *Solanum*, *Echinochloa*, *Scirpus*, *Monochoria*, *Sagittaria*, *Bromus*, *Alopecurus*, *Sorghum halepense*, *Rottboellia*, *Cyperus*, *Abutilon*, *Sida*, *Xanthium*, *Amaranthus*, *Chenopodium*, *Ipomoea*, *Chrysanthemum*, *Galium*, *Viola*, and *Veronica*.

The compounds of formula I may also be used in combination with a co-herbicide. Suitable co-herbicides are, for example, ametryn, atrazine, hexazinone, asulam, diuron, 2,4-D, halosulfuron, fluometuron, prometryn, metolachlor, α -metolachlor, norflurazon, pyrithiobac-sodium, DSMA, MSMA, trifluralin, pendimethalin, bromoxynil, glyphosate, glufosinate and clomazone.

The invention is illustrated by the following non-limitative Examples.

Formulation examples

F1. Coated granulates

	a)	b)	c)
Active ingredient of formula I	0.1 %	5 %	15 %
Polyethylene glycol mw 200	1.0 %	2 %	3 %
Highly dispersed silicic acid	0.9 %	1 %	2 %
Inorganic carrier (Ø 0.1–1 mm) such as CaCO_3 or SiO_2	98.0 %	92 %	80 %

The finely ground active substance is uniformly applied in a mixer to the carrier moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

F2. Extruder granulates

	a)	b)	c)	d)
Active ingredient of formula I	0.1 %	3 %	5 %	15 %
Sodium ligninsulfonate	1.5 %	2 %	3 %	4 %
Carboxymethylcellulose	1.4 %	2 %	2 %	2 %
Kaolin	97.0 %	93 %	90 %	79 %

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The compound is mixed and ground with the adjuvants, and the mixture is moistened with water. This mixture is extruded and then dried in a stream of air.

<u>F3. Dusts</u>	a)	b)	c)
Active ingredient of formula I	0.1 %	1 %	5 %
Talc	39.9 %	49 %	35 %
Kaolin	60.0 %	50 %	60 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding on a suitable mill.

Example F4: Preparation of a wettable granulate of the compound of formula I:

The following substances are admixed and subsequently ground using a conventional mill.

- 75 % A-crystal modification of the compound of formula I
- 4 % dibutylnaphthalenesulfonic acid sodium salt
- 8 % sodium lignin sulfonate
- 0.5 % silicone defoamer
- ad 100 % silicon dioxide

The mixture is subsequently mixed with 22-26 % by weight water and granulated. After drying on a commercial continuous drier to a residual moisture of < 4.5 %, the granulate obtained is sieved (vibration/tumbler sieve) to a grain size of 0.4 to 1.6 mm. Granulates are obtained, which contain the compound of formula I as the C-crystal modification.

Example F5: Preparation of a wettable granulate of the compound of formula I:

The following substances are admixed and subsequently ground using a conventional mill.

- 75 % B-crystal modification of the compound of formula I
- 4 % dibutylnaphthalenesulfonic acid sodium salt
- 8 % sodium lignin sulfonate
- 0.5 % silicone defoamer
- ad 100 % silicon dioxide

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The mixture is subsequently mixed with 18-20% by weight water and granulated. After drying on a commercial continuous drier to a residual moisture of < 4.5 %, the granulate obtained is sieved (vibration/tumbler sieve) to a grain size of 0.4 to 1.6 mm. Granulates are obtained, which contain the compound of formula I as the B-crystal modification.

Example F6: Preparation of a wettable granulate of the compound of formula I:

The following substances are admixed and subsequently ground using a conventional mill.

75 %	K-crystal modification of the compound of formula I
4 %	dibutylphthalenesulfonic acid sodium salt
8 %	sodium lignin sulfonate
0.5 %	silicone defoamer
ad 100 %	silicon dioxide

The mixture is subsequently mixed with 43-48% by weight water and granulated. After drying on a commercial continuous drier to a residual moisture of < 4.5 %, the granulate obtained is sieved (vibration/tumbler sieve) to a grain size of 0.4 to 1.6 mm. Granulates are obtained, which contain the compound of formula I as a mixture of the B-crystal modification and the C-crystal modification.

The X-ray powder pattern indicates the d-values (interlattice plane intervals), the associated intensities of the X-ray reflexes and the angle of refraction 2theta (apparatus-specific) of the corresponding crystal modification.

Measurement of the X-ray powder pattern was effected with an Enraf-Nonius Guinier camera FR 552 using CuKalpha1 radiation. The diagrams recorded on X-ray film were evaluated on a Johansson Line-Scanner LS-18 using Scanpi-Software.

Preparation Examples:

Example P1: Preparation of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification):

A solution of 40 g of 4,6-dimethoxy-pyrimidine-2-isocyanate in 300 g of tetrahydrofuran (water-free) is added at a temperature of 40-45°C to a suspension of 59 g of 3-(2-trifluoroethoxy)-pyridin-ylsulfonamide sodium salt in 210 g of water-free tetrahydrofuran.

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The reaction mixture is subsequently stirred at a temperature of 40°C until conversion is complete. The J-modification is finally obtained by filtering and washing with water-free tetrahydrofuran.

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Table X1: X-ray powder pattern of modification J:

<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
5.6	15.7	weak
8.6	10.2	very stark
10.7	8.2	weak
11.3	7.8	weak
12.1	7.3	weak
13.1	6.7	weak
13.6	6.5	very weak
14.4	6.2	average
15.7	5.64	very weak
16.0	5.53	weak
16.3	5.42	weak
17.4	5.09	weak
17.9	4.96	average
18.2	4.86	very weak
19.3	4.60	average
20.3	4.37	average
21.0	4.24	weak
21.6	4.11	very stark
22.5	3.95	very weak
22.8	3.90	weak
23.3	3.81	very weak
24.0	3.71	average
24.5	3.62	weak
25.3	3.52	very weak
26.0	3.43	stark
26.4	3.37	weak
26.8	3.32	very weak
27.3	3.27	weak
30.4	2.94	very weak
31.7	2.82	average

Example P2: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (K-modification):

The K-modification is obtained by drying the J-modification of example P1 at a temperature of 60°C and at a pressure of 0.04 bars. This crystal form is water-free and solvent-free: thermogravimetric measurement at 175°C shows a weight loss of less than 0.1 % by weight.

Table X2: X-ray powder pattern of modification K:

<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
6.6	13.4	weak
8.8	10.1	very weak
9.5	9.3	very strong
11.4	7.8	weak
12.9	6.9	very weak
13.3	6.7	very weak
15.7	5.63	very weak
16.6	5.35	average
19.0	4.66	weak
20.0	4.44	very weak
20.4	4.35	weak
21.5	4.12	strong
22.6	3.94	strong
22.9	3.87	very weak
23.7	3.76	weak
24.6	3.61	average
25.5	3.49	very weak
26.2	3.40	very weak

Example P3: Preparation of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1 (I-modification):

A solution of 19.9 g of 4,6-dimethoxy-pyrimidine-2-isocyanate in 350 g of tetrahydrofuran (water-free) is added at a temperature of 25 °C to a suspension of 34.2 g of 3-(2-trifluoroethoxy)-pyridin-ylsulfonamide sodium salt in 200 ml of water-free tetrahydrofuran. The reaction mixture is stirred at a temperature of 25°C until conversion is complete. Then,

10 g of water are added and the mixture stirred for 18 hours. The I-modification is finally obtained by filtering and washing with water-free tetrahydrofuran.

Table X3: X-ray powder pattern of modification I:

<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
7.6	11.6	weak
9.0	9.8	very weak
11.0	8.0	very strong
11.6	7.6	average
13.3	6.7	strong
13.7	6.4	very weak
14.0	6.3	weak
14.4	6.1	very weak
15.3	5.80	average
15.6	5.66	very weak
16.2	5.47	strong
17.3	5.12	very weak
17.4	5.08	very weak
18.3	4.84	weak
18.6	4.76	weak
19.8	4.47	strong
20.1	4.40	weak
21.1	4.21	average
21.2	4.19	average
21.4	4.15	very weak
22.2	4.00	very weak
22.6	3.93	very weak
23.2	3.84	average
23.9	3.72	very strong
24.8	3.58	average
25.3	3.52	average
26.9	3.32	very weak
27.2	3.28	very weak

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<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
27.5	3.25	very weak
28.7	3.11	very weak
29.0	3.07	very weak
30.2	2.95	very weak
31.2	2.86	weak
31.7	2.82	very weak
32.6	2.75	very weak
34.9	2.57	weak
36.0	2.49	very weak

Example P4: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1 (B-modification):

The B-modification is obtained selectively by suspending 100 g of the K-modification prepared in example P2 in 230 g of water for 15 minutes, then seeding preferably with 1-3 g of seed crystals of the B-modification, and stirring the suspension at a temperature of 20-25 °C until transformation is complete. The suspension is subsequently filtered and the residue of filtration dried at a temperature of 60°C and at a pressure of 0.04 bars until attaining a constant weight.

Table X4: X-ray powder pattern of modification B:

<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
8.9	10.0	average
9.6	9.2	strong
10.3	8.6	very weak
11.0	8.1	weak
12.2	7.2	strong
12.9	6.9	strong
13.8	6.4	average
15.2	5.82	strong
15.4	5.75	strong
15.7	5.64	very strong

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2θ[degree] d[Å] Intensity

16.0	5.53	very weak
17.3	5.13	average
17.8	4.97	very strong
19.1	4.65	average
20.6	4.30	very strong
21.0	4.22	weak
21.4	4.15	very weak
22.1	4.02	weak
22.5	3.94	weak
23.4	3.79	average
23.8	3.73	weak
24.2	3.68	average
24.6	3.61	weak
24.8	3.58	weak
25.3	3.52	very strong
26.0	3.42	very weak
26.4	3.37	weak
26.9	3.31	very weak
27.3	3.27	very weak
27.6	3.23	weak
28.0	3.18	average
28.9	3.08	very weak
29.4	3.03	very weak
30.3	2.95	very weak
31.2	2.87	strong
31.7	2.82	very weak
32.1	2.79	very weak
32.7	2.73	very weak
33.4	2.68	very weak
33.8	2.65	very weak
34.0	2.63	very weak
34.5	2.60	weak

2θ[degree] d[Å] Intensity

34.9 2.57 weak

The crystals forms A, C, F, I and J can also be transformed into the B form in analogous manner. In doing so, these crystal forms may also still be moist with solvent. In this case, the amount of water can be increased slightly.

Example P5: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (C-modification):

100 g of the K-modification produced in example P2 are mixed with 20 g of water for the duration of 3 hours and subsequently dried at a temperature of 60°C and at a pressure of 0.04 bars.

Table X5: X-ray powder pattern of modification C:2θ[degree] d[Å] Intensity

6.7	13.1	average
8.1	11.0	very strong
10.1	8.8	weak
11.4	7.7	very strong
12.2	7.2	very strong
12.7	7.0	weak
13.9	6.4	weak
14.3	6.2	strong
14.9	5.96	weak
15.0	5.90	weak
15.7	5.64	strong
16.2	5.47	weak
16.6	5.34	average
17.1	5.19	weak
18.5	4.79	weak
18.7	4.74	average
19.1	4.64	very weak

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2θ[degree] d[Å] Intensity

19.5	4.55	strong
19.9	4.47	weak
20.4	4.35	strong
20.8	4.26	average
21.5	4.13	weak
21.9	4.06	very weak
22.7	3.92	very strong
23.0	3.87	weak
23.5	3.79	very strong
24.2	3.67	weak
24.6	3.61	average
24.9	3.58	strong
25.7	3.47	weak
26.9	3.32	very weak
27.5	3.24	average
28.4	3.14	weak
28.6	3.12	weak
29.1	3.07	weak
29.3	3.04	strong
30.1	2.97	very weak
30.6	2.92	very weak
31.0	2.88	weak
31.7	2.82	weak
32.3	2.77	very weak
32.7	2.74	very weak
33.3	2.69	weak
33.7	2.66	very weak

Example P6: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, in essentially amorphous form (A-modification):

1.56 g of N-[(4,6-dimethoxy-2-pyrimidinyl)carbamoyl]-3-(2,2,2-trifluoroethoxy)-pyridin-2-sulfonamide are added at a temperature of 20°C to a solution of 40 ml of aqueous 0.1 N

sodium hydroxide. The reaction mixture is stirred for 18 hours at a temperature of 20°C. The residue obtained after concentrating by evaporation under vacuum at a temperature of 50° C is subsequently stirred with ether and filtered. The A-modification is obtained by drying the filtrate at elevated temperatures (>120°C).

Example P7: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (C-modification) from the A-modification:

Crystals of the A-modification are exposed to an atmosphere of 98% relative humidity for 4 hours at a temperature of 20°C. The C-modification is obtained with the crystallographic data given in example P5.

Example P8: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 2, L is dioxane and s is 0 (G-modification):

15 g of the A-modification produced e.g. as in example P6 are stirred in 85 g of dioxane for 2½ days at a temperature of 20°C and the mixture subsequently filtered. After filtration, the G-modification is obtained as the residue of filtration with the X-ray crystallographic data given in Table X8.

Table X8: X-ray powder pattern of modification G:

<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
5.8	15.3	strong
7.0	12.7	very weak
8.4	10.5	weak
11.1	7.9	average
12.8	6.9	average
13.4	6.6	very weak
14.3	6.2	very strong
14.9	5.96	average
17.4	5.08	average
17.8	4.98	weak
18.3	4.84	average

<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
19.3	4.60	average
19.7	4.51	average
19.8	4.47	very weak
20.8	4.27	weak
21.0	4.23	average
22.3	3.98	average
22.7	3.91	average
23.3	3.81	weak
23.9	3.71	strong
24.4	3.65	average
24.9	3.57	weak
25.4	3.50	average
26.2	3.39	very weak
26.7	3.33	weak
28.9	3.08	very weak
29.5	3.02	very weak
30.5	2.93	weak

Example P9: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 1, L is dioxane and s is 0 (F-modification):

The F-modification is obtained by exposing the G-modification produced in example P8 to an atmosphere of 50% relative humidity for a period of 8 days at a temperature of 20-25°C.

Table X9: X-ray powder pattern of modification G:

<u>2θ[degree]</u>	<u>d[Å]</u>	<u>Intensity</u>
6.0	14.7	very weak
7.0	12.6	very weak
8.1	10.9	average
11.4	7.8	average

2θ[degree] d[Å] Intensity

12.0	7.4	very weak
12.7	7.0	weak
13.4	6.6	weak
14.3	6.2	weak
16.2	5.45	strong
18.0	4.91	average
18.4	4.83	weak
18.6	4.76	very weak
20.8	4.28	very weak
21.7	4.10	weak
22.2	4.00	very weak
23.7	3.75	very strong
24.7	3.60	very weak

Biological Examples

Example B1: Post-emergent herbicidal action

The test plants are sown in standard soil in plastic pots in a greenhouse, and sprayed at the 2- to 3-leaf stage with an aqueous suspension of the test compounds of formula I prepared from a 25% wettable powder [example F3, b) of WO 97/34485] of the test compounds of formula I, at a dosage of 7.5 g/ha. The test plants are then further cultivated in the greenhouse under optimum conditions. After ca. 21 days test duration, the test is evaluated (100 = total damage, 0 = no damage). Table 1 shows the results obtained.

Table 1: Post-application on cotton

test plants	K-modification
cotton	15
Ipomea	90
Xanthium	100
Cassia	98

Example B2: Post-emergent herbicidal action

The test plants are sown in standard soil in plastic pots in a greenhouse, and sprayed at the 2- to 3-leaf stage with an aqueous suspension of the test compounds of formula I prepared from a 75% wettable granulate (example F4 for the A-modification or example F5 for the B-modification) of the test compounds of formula I, at a dosage of 7.5 g/ha. The test plants are then further cultivated in the greenhouse under optimum conditions. After ca. 21 days test duration, the test is evaluated (100 = total damage, 0 = no damage). Table 2 shows the results obtained.

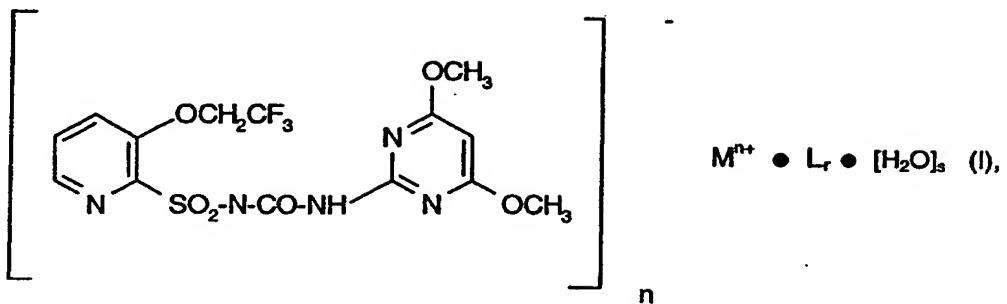
Table 2: Post-application on cotton

test plants	A-modification	B-modification
cotton	5	0
Ipomea	80	75

The same results are obtained by formulating the compounds of formula I in accordance with Examples F2 and F6 to F8 of WO 97/34485.

What is claimed is:

1. Compounds of formula I



wherein

M is an alkali metal or an alkaline earth metal;

n is 1 or 2;

r and **s**, independently of one another, are 0, $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$ or 3; and

L is ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, methylene chloride, trichloromethane, trichloroethane, tetrahydrofuran, diethylether, 1,2-dimethoxyethane, dioxane, methyl-tert.-butylether, chlorobenzene, toluene or xylene, with the provision that **r** is other than $1\frac{1}{2}$ if **L** is dioxane and **s** is 0.

2. Compounds of formula I according to claim 1, in which **M** is sodium, potassium, magnesium or calcium.

3. Compounds of formula I according to claim 1, in which **L** is dioxane, tetrahydrofuran or water.

4. Compounds of formula I according to claim 1, in which **n** is 1 and **M** is sodium.

5. Compounds of formula I according to claim 1, in which **M** is sodium, **n** is 1, **r** is 0 and **s** is 0.

6. Compounds of formula I according to claim 1, selected from

- the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 10.0/average; 9.2/strong; 8.6/very weak; 8.1/weak; 7.2/strong; 6.9/strong; 6.4/average; 5.82/strong; 5.75/strong; 5.64/very strong; 5.53/very weak; 5.13/average; 4.97/very strong; 4.65/average; 4.30/very strong; 4.22/weak; 4.15/very weak; 4.02/weak; 3.94/weak; 3.79/average; 3.73/weak; 3.68/average; 3.61/weak; 3.58/weak; 3.52/very strong; 3.42/very weak; 3.37/weak; 3.31/very weak; 3.27/very weak; 3.23/weak; 3.18/average; 3.08/very weak; 3.03/very weak; 2.95/very weak; 2.87/strong; 2.82/very weak; 2.79/very weak; 2.73/very weak; 2.68/very weak; 2.65/very weak; 2.63/very weak; 2.60/weak; 2.57/weak;
- the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0, characterised by the X-ray powder pattern with d[Å]/intensity: 5.7/weak; 10.2/very strong; 8.2/weak; 7.8/weak; 7.3/weak; 6.7/weak; 6.5/very weak; 6.2/average; 5.64/very weak; 5.53/weak; 5.42/weak; 5.09/weak; 4.96/average; 4.86/very weak; 4.60/average; 4.37/average; 4.24/weak; 4.11/very strong; 3.95/very weak; 3.90/weak; 3.81/very weak; 3.71/average; 3.62/weak; 3.52/very weak; 3.43/strong; 3.37/weak; 3.32/very weak; 3.27/weak; 2.94/very weak; 2.82/average;
- the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, characterised by the X-ray powder pattern with d[Å]/intensity: 13.4/weak; 10.1/very weak; 9.3/very strong; 7.8/weak; 6.9/very weak; 6.7/very weak; 5.63/very weak; 5.35/average; 4.66/weak; 4.44/very weak; 4.35/weak; 4.12/strong; 3.94/strong; 3.87/very weak; 3.76/weak; 3.61/average; 3.49/very weak; 3.40/very weak;
- the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 13.1/average; 11.0/very strong; 8.8/weak; 7.7/very strong; 7.2/very strong; 7.0/weak; 6.4/weak; 6.2/strong; 5.96/weak; 5.90/weak; 5.64/strong; 5.47/weak; 5.34/average; 5.19/weak; 4.79/weak; 4.74/average; 4.64/very weak; 4.55/strong; 4.47/weak; 4.35/strong; 4.26/average; 4.13/weak; 4.06/very weak; 3.92/very strong; 3.87/weak; 3.79/very strong; 3.67/weak; 3.61/average; 3.58/strong; 3.47/weak; 3.32/very weak; 3.24/average; 3.14/weak; 3.12/weak; 3.07/weak; 3.04/strong; 2.97/very weak; 2.92/very weak; 2.88/weak; 2.82/weak; 2.77/very weak; 2.74/very weak; 2.69/weak; 2.66/very weak; and

- the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 1.6/weak; 9.8/very weak; 8.0/very strong; 7.6/average; 6.7/strong; 6.4/very weak; 6.3/weak; 6.1/very weak; 5.80/average; 5.66/very weak; 5.47/strong; 5.12/very weak; 5.08/very weak; 4.84/weak; 4.76/weak; 4.47/strong; 4.40/weak; 4.21/average; 4.19/average; 4.15/very weak; 4.00/very weak; 3.93/very weak; 3.84/average; 3.72/very strong; 3.58/average; 3.52/average; 3.32/very weak; 3.28/very weak; 3.25/very weak; 3.11/very weak; 3.07/very weak; 2.95/very weak; 2.86/weak; 2.82/very weak; 2.75/very weak; 2.57/weak; 2.49/very weak.

7. A compound of formula I according to claim 1, wherein

M is sodium, n is 1, r is 0 and s is 0 (K-modification), produced by drying the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification), at a temperature of 35°C to 65°C in a vacuum.

or wherein

M is sodium, n is 1, r is 0 and s is 1 (C-modification), produced by either

contact of the essentially amorphous form (A-modification) by air of 98% relative humidity or mixing the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, with water in a ratio of water to the K-modification of 0.1 : 1 to 0.4 : 1 and separating and drying the product obtained at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;

or wherein

M is sodium, n is 1, r is 0 and s is 1 (B-modification), produced by adding water to the compound of formula I, in which M is sodium, n is 1 and L, r and s are defined as in formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, then filtering and the drying the residue of filtration at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

8. A method for the preparation of compounds of formula I according to claim I, whereby in order to produce the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0, a 5-35% by weight solution of 4,6-dimethoxy-

pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran;

in order to produce the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, a 5-35% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, then filtered, and the residue of filtration (J-modification) is subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;

in order to produce the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, either the essentially amorphous form (A-modification) is exposed to an atmosphere of 98% relative humidity, or the K-modification is mixed with water in a ratio of water to K-modification of 0.1 : 1 to 0.4 : 1, then filtered, and the residue of filtration subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;

in order to produce the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, a 5-35% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 0-30°C to a 10-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, and subsequently 1-20 molar equivalents of water, based on the 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt, are added; and

in order to produce the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, water is added to the compound of formula I, in which M is sodium, n is 1 and L, r and s are defined as in formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, then filtration takes place and the residue of filtration is dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

9. A herbicidal and plant growth inhibiting composition, which comprises a herbicidally effective amount of the compound of formula I on an inert carrier.

10. Composition according to claim 9, which contains a co-herbicide.

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11. A method of controlling undesirable plant growth, which comprises treating the plants or the locus thereof with a herbicidally effective amount of an active ingredient of formula I or of a composition containing such an active ingredient.

12. A method of inhibiting plant growth, which comprises treating the plants or the locus thereof with a herbicidally effective amount of an active ingredient of formula I or of a composition containing such an active ingredient.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/01627

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C07D401/12 A01N47/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 41112 A (CIBA GEIGY AG ;FOERY WERNER (CH)) 6 November 1997 (1997-11-06) cited in the application the whole document	1-12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the International search report
8 June 2000	11/07/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer De Jong, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/01627

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9741112 A	06-11-1997	AU HR	2696997 A 970212 A	19-11-1997 30-04-1998

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